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DIETHYL ESTER OF CYCLOHEXANONE-2-PHOSPHINIC ACID

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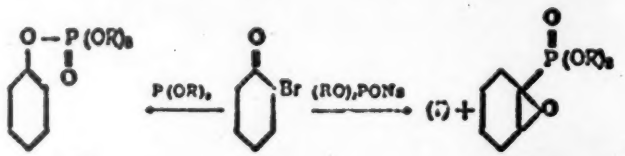
Esters of cyclohexanone-2-phosphinic acid are of great interest for studying the possibility of a keto-enol tautomerism as analogs of cyclohexanone-2-carboxylic ester, whose tautomerism has been studied thoroughly.

Attempts which we made to prepare the ester of cyclohexanone-2-phosphinic acid by the normal methods for synthesizing phosphinic esters did not lead to the desired results.

Both in the case of chlorocyclohexanone and in the case of bromocyclohexanone, the Arbuzov rearrangement led to the formation of the cyclohexenyl ester of phosphoric acid.

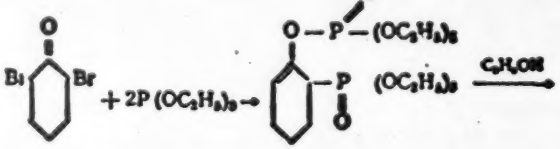
The Michaelis-Becker reaction gave ester (I) together with the ester of epoxycyclohexanephosphinic acid (II).



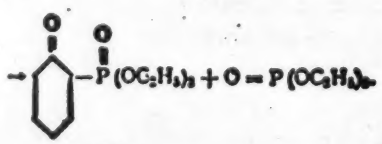
(I) (II)

We were able to synthesize diethyl cyclohexanone-2-phosphinate in the following way. As is known [1,2], α,α'-dihaloketones react with trialkyl phosphites with the formation of the dialkylphosphoric ester of the enol form of the β-ketophosphinic ester, which gives the β-ketophosphinic ester on transesterification with alcohol.

We achieved an analogous reaction starting from α,α'-dibromocyclohexanone



(III)



(IV)

The action of triethyl phosphite on α,α'-dibromocyclohexanone yielded the diethylphosphoric ester of the enol form of cyclohexanone-2-phosphinic ester (III) with the following constants: b. p. 172.5-173°/2.5 mm; d_4^{20} 1.1835; n_D^{20} 1.4652.

The Raman spectrum of the diethylphosphoric ester of the enol form of cyclohexanone-2-phosphinic ester (III) contained the following frequencies* (cm^{-1}): 645(0), 703(1), 748(2), 805(1), 850(0), 940(0), 1040(0), 1095(3), 1174(0), 1225(1), 1280(1), 1393(0), 1443(3 broad), 1675(3), 2720(1), 2870(3), 2898(2), 2931(5 broad), 2972(5), 3054(0).

Among the frequencies in the spectrum we should note the frequency of the valence oscillation of the C = C group, 1675 cm^{-1}, and the very weak frequency of the C – H group at the double bond, 3054 cm^{-1}. Transesterification of ester (III) with ethyl alcohol led to the diethyl ester of cyclohexanone-2-phosphinic acid (IV) with the following constants: b. p. 119-121°/3.5 mm; d_4^{20} 1.1258; n_D^{20} 1.4654; MR_D found 57.56.

The cyclohexanonephosphinic ester was found to be an interesting compound. Its molecular refraction lay between the values calculated for the ketone form (IV) (57.06) and the enol form (V) (58.11).

With ferric chloride in alcohol solution, the compound gave an intense violet-red color, characteristic of enols.

The presence of enolization was confirmed by titrating the cyclohexanonephosphinic ester with bromine in the presence of β-naphthol by Meyer's method [4]. Titration in an alcohol medium gave 9% enol. Titration in a hexane medium gave 60% enol.

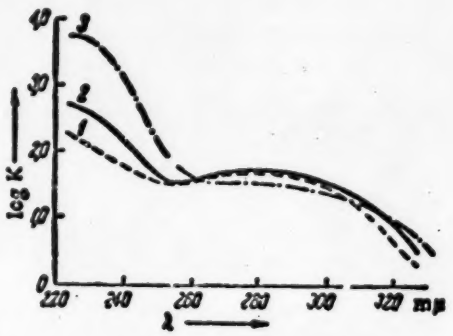
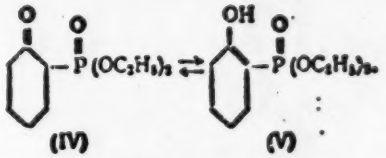


Fig. 1. UV absorption spectra of diethyl cyclohexanone-2-phosphinate in solution 1) in H_2O, C = 0.01446; 2) in CH_3OH, C = 0.01866; 3) in isooctane, C = 0.02310.

Thus, as in the case of cyclohexanone-2-carboxylic esters and other β-dicarbonyl compounds, the equilibrium is strongly displaced towards the enol form in the non-polar solvent hexane [5].

The data presented indicate the presence of keto – enol tautomerism in cyclohexanone-2-phosphinic ester



(IV) (V)

The presence of tautomerism was also confirmed by spectroscopic measurements.

The Raman spectrum of the diethyl ester of cyclohexanone-2-phosphinic acid contained the following frequencies (cm^{-1}): 242(1 diff.), 272(1 diff.), 337(2 broad), 385(1diff.), 446(1), 479(2), 525(1), 602(3), 658(5), 707(2), 753(2), 792(2), 824(3), 852(5), 900(0), 958(4), 986(0), 1025(3 broad), 1053(0), 1078(1), 1101(3), 1119(2), 1135(2), 1180(4), 1225(1), 1246(1), 1282(2), 1356(2), 1396(1), 1422(6), 1451(7), 1662(0), 1711(3), 2720(0), 2867(5), 2900(3), 2934(6 broad), 2973(4 diff.).

As can be seen from the spectrum presented, the frequency 1711 cm^{-1} indicates the presence of a keto group, which may belong to the keto form (IV). The intense frequency 1631 cm^{-1} must pertain to the presence of a C = C grouping, indicating the presence of the enol form (V). A study of the ultraviolet absorption spectrum confirmed the conclusions on the presence of keto and enol forms of diethyl cyclohexanone-2-phosphinate, arrived at on the basis of chemical and Raman spectral data.

*The spectrum had a dark background. We were unable to improve the spectrum by redistilling the substance in an Arbuzov flask and in the cell before photographing the spectrum.

Figure 1 shows the UV absorption spectrum of diethyl cyclohexanone-2-phosphinate in water (curve 1), methyl alcohol (curve 2), and isooctane (curve 3). The absorption spectrum of diethyl cyclohexanone-2-phosphinate has two absorption maximas: 280 mμ, corresponding to absorption of the C = O group of the keto form (IV) and a mixmum at ~220 mμ.

In isooctane solution, there is a small fall in absorption for the maximum at 280 mμ. The molecular absorption coefficient in the region of ~220 mμ depends strongly on the nature of the solvent: the smallest value is observed in aqueous solution (log K = 2.32), and this increases in methyl alcohol (log K = 2.75), and rises considerably in isooctane (log K = 3.75).

Thus, the effect of the polarity of the solvent on the molecular absorption coefficient was similar to that in the case of acetoacetic ester [5] and other compounds showing keto – enol tautomerism.

Figure 2 shows the UV absorption spectra of diethyl cyclohexanone-2-phosphinate in methyl alcohol, containing sodium methylate. In an alkaline medium, the spectrum of diethyl cyclohexanone-2-phosphinate showed a maximum at 250 mμ, corresponding to the formation of enolate ions (Fig. 2, 1 and 2).

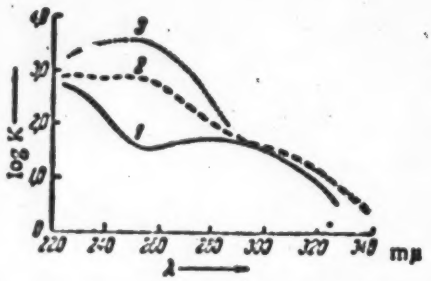


Fig. 2. U. V. absorption spectra of diethyl cyclohexanone-2-phosphinate in methyl alcohol: 1) C = 0.01866, 2) the same + CH_3ONa, $C_{subst.}$ = 0.01671, C_{CH_3ONa} = 0.01653; 3) the same + CH_3ONa, $C_{subst.}$ = 0.01656, C_{CH_3ONa} = 0.08983.

The maximum was shifted with respect to the maximum corresponding to the enol form (V) by approximately 30 mμ. A similar shift was observed for certain 1,3-diketo derivatives of cyclohexane [6]. As can be seen, the value of the maximum depends on the sodium methylate concentration. It is interesting to note that the diethyl ester of phosphonoacetone shows an analogous absorption maximum in the presence of sodium methylate, as we noted previously [7].

Thus, the possibility of a keto-enol tautomerism in esters of phosphinic acids with a keto group in a β-position in the hydrocarbon radical attached to the phosphorus was demonstrated on the example of diethyl cyclohexanone-2-phosphinic ester.

EXPERIMENTAL

Action of triethyl phosphite on α,α'-dibromocyclohexanone. Triethyl phosphite (52 g) was added dropwise to 49 g of dibromocyclohexanone [8] (b. p. 123-126°/6 mm) at room temperature. At first there was strong heat evolution and ethyl bromide distilled. Subsequently, the addition of phosphite did not cause strong heat evolution. Finally, the flask was heated for 1 hour at 150-155° and 1 hour at 185-190°. Ethyl bromide was liberated during the heating. A total of 27.6 g of ethyl bromide was liberated (theoret., 34 g). Distillation from an Arbuzov flask gave the following fractions: 1) 48-100°/2.5 mm, 9 g; 2) 100-160°/2.5 mm, 14.9 g; 3) 160-179°/2.5 mm, 31.8 g.

Subsequent distillation of the third fraction with a Widmer column gave a substance (16.7 g) with the following constants: b. p. 172.5-173°/2.5 mm; d_4^{20} 1.1885; n_D^{20} 1.4652; MR_D found 86.19, $C_{14}H_{28}O_7P_2F_2$ calculated 87.05.

	Found %	P 16.97
$C_{14}H_{28}O_7P_2$.	Calculated %	P 16.75

Transesterification of the product with b. p. 172.5-173°/2.5 mm. To an alcohol solution of sodium ethylate prepared from 0.3 g of sodium and 30 ml of absolute alcohol was added 12.7 g of product with b. p. 172.5-173°. The flask, which was fitted with a Widmer column, was heated on a water bath for 2 hours. The reaction mixture was neutralized with glacial acetic acid (1 ml), the alcohol removed and the residue vacuum distilled.

Fractions were obtained: 1. 66-76°/6.5 mm, 4.9 g, and 2. 110-116°/3 mm, 4.5 g.

Redistillation of the first fraction yelided triethyl phosphate with b. p. 66-66.5°/2.5 mm; d_4^{20} 1.0733; n_D^{20} 1.4048. Distillation of the second fraction yielded a substance (3.5 g) with the following constants: b. p. 119-121°/3.5 mm; d_4^{20} 1.1258; n_D^{20} 1.4654; MR_D found 57.56, $C_{10}H_{19}O_4P$ calculations: keto form 57.06; enol form 58.11.

$C_{10}H_{19}O_4P$. Found %: P 13.20; 13.48
Calculated %: P 13.24

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STUDY OF PHASE CHANGES OF URANIUM OXIDES IN AIR

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S. G. Tresvyatskii, and V. I. Kushakovskii

The present work was carried out in connection with contradictory information [1-6] on the decomposition of urano-uranic oxide on heating.

EXPERIMENTAL

1. Determination of the decomposition point of urano-uranic oxide in air. We determined the decomposition point of urano-uranic oxide in air by continuously weighing it in the form of tablets or powder while it was heated from room temperature to 1600-1900°. We heated the oxides to 1600-1700° in platinum crucibles and to higher temperatures in beryllium oxide crucibles. The temperature was measured with a platinum-platinorhodium thermocouple and with an optical pyrometer with a vanishing filament. To heat samples we used a

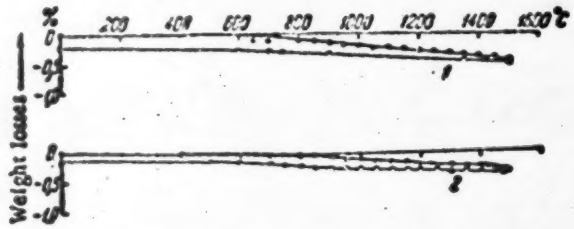

Fig. 1. Curves of the change in weight of U_3O_8 on heating and cooling in a Kryptol furnace: 1) experiment No. 4 in an open platinum crucible; 2) experiment No. 6 in a closed platinum crucible.

a Silit furnace, a Kryptol furnace or a Tamman type furnace. In the latter case, in order to create an air atmosphere inside the furnace, a beryllium oxide tube was inserted and argon was passed between the carbon tube (internal diameter 60 mm) and the beryllium oxide tube (internal diameter 34 mm). For continuous weighing of the samples, we used analytical balances, whose sensitivity equaled 0.0005-0.001 g due to the gas streams in the furnace. We estimated the accuracy of the weighing as ±0.001 g. A sample of 6-8 g was usually taken. The maximum loss of weight due to the elimination of oxygen for such samples was 0.2-0.3 g and was detected with sufficient accuracy. All the experiments lasted for about the same time, namely, 8 hours. Figures 1 and 2 show the curves of the change in weight of urano-uranic oxide on heating and cooling in air.

When urano-uranic oxide was heated to 1400° in a Silit furnace, we obtained curves similar to those in Fig. 1 and with heating to 1800° in a Tamman type furnace, curves similar to those in Fig. 2. The similarity of the curves obtained with different types of furnace indicates that the composition of the gases in the furnaces were close to the composition of air in all cases.

As follows from the curves in Figs. 1 and 2, rapid decomposition of uranium oxide begins at 1500° and the phase thus formed absorbs oxygen at temperatures below this. However, the weight of the sample never returned to the initial value, indicating the volatility of the uranium oxides. The volatility was noticeable when urano-uranic oxide was heated to 1500° and in this case 0.1-0.2% was lost. With heating to 1600-1700°, the volatilization loss from a closed crucible was 0.3% and from an open crucible, 0.6-0.7%. When uranium oxides were heated above 1700°, the volatility increased considerably so that with heating to 1800° the loss was 3-4% and at 1900-1950° the sample evaporated almost completely over a short period (10-20 minutes). The decomposition of 7-8 g of urano-uranic oxide liberated about 200-250 cc of oxygen. The volume of the crucible used in the experiments was 5-7 cc. Therefore, it can be assumed that the oxygen liberated during dissociation carried nitrogen from the crucible with it and this led to an increase in the partial pressure of oxygen, whose value tended to 1 atm during the decomposition process.

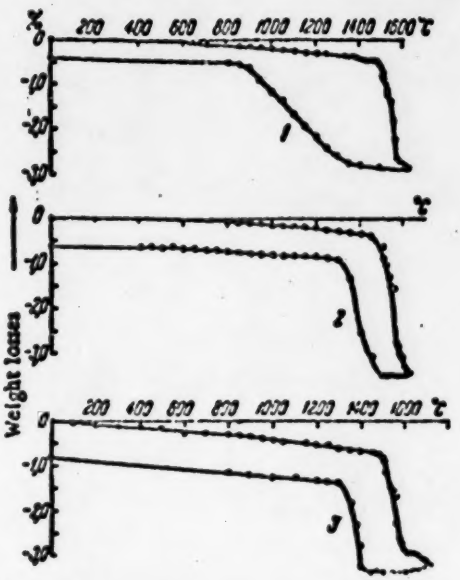

Fig. 2. Curves of the change in weight of U_3O_8 on heating and cooling in a Kryptol furnace: 1) experiment No. 2 in a closed platinum crucible; 2) experiment No. 5 in an open platinum crucible; 3) experiment No. 13 in an open beryllium oxide crucible.

2. Determination of phase composition of dissociation products of urano-uranic oxide. It was not possible to estimate the degree of reduction of urano-uranic oxide with sufficient accuracy from the curves of the change in weight due to the volatility of not only oxygen, but also the uranium oxides themselves. Therefore, quenched samples were used for determining the phase composition at various temperatures. The samples were heated as indicated above and quenched by dumping the samples with crucible into ice and water. The phase composition of the quenched samples was determined by taking x-ray powder pictures with copper K_α radiation in cameras 85 mm in diameter. The ratio of O:U was calculated from the increase in weight of the quenched samples after they had been fired in air at 700-800° for 1 hour. It was assumed that the oxidation product was U_3O_8 of stoichiometric composition. The results of the investigations are presented in Table 1.

From the results of the 2nd series of experiments described it may be concluded that when heated in air, urano-uranic oxide begins to lose oxygen noticeably even at 900°, but up to 1450° the amount of oxygen in the oxide still corresponds to the formula $UO_{2.63}$. The x-ray picture of an oxide of this composition differed from that obtained with U_3O_8. Calculation of the lattice parameters of $UO_{2.63}$ as an orthothombic phase gave the following values: a = 6.713kX; b = 3.957 kX; c = 4.145 kX. According to our calculations, the corresponding periods for U_3O_8 equal: a = 6.714 kX; b = 3.966kX; c = 4.161 kX. The accuracy of the determination of the lattice parameters was ±0.002-0.003 kX. We detected two phases x-radiographically in a sample quenched from 1500°: U_3O_8 and, apparently, the $UO_{2.6}$-phase. At higher temperatures, right up to the melting point, U_3O_8 was found in equilibrium with oxygen at atmospheric pressure. With an increase in temperature the oxygen content of this oxide decreased and, in its turn, this produced an increase in the lattice period (see Fig. 3).

Fig. 3. Dependence of U_3O_8 lattice period on oxygen content.

The results obtained made it possible for us to add to the high-temperature region of the U-O phase diagram constructed by Akkermann [2] from the results of investigations by various authors (see Fig. 4).

TABLE 1

Results of Investigating Quenched Samples

Sample No.	Starting oxide	Heat treatment conditions: medium or type of furnace	temp. °C	retention time, min.	cooling conditions	Final composition	Results of x-ray analysis: latt. per. of cubic phase, kX	phase present
1	UO_3	Vacuum 10^{-2}	2000	60	In furn.	$UO_{2.0}$	5,4597	UO_2
2	U_3O_8	Air	800	300	The same	$UO_{2.667}$		α-U_3O_8
3	same	Kryptol furnace	1400	60	Quenched in H_2O	$UO_{2.62}$		$UO_{2.6}$-phase*
4	"	"	1450	180	" "	$UO_{2.62}$		$UO_{2.6}$-phase
5	"	"	1500	20	" "	$UO_{2.62}$	5,428	U_4O_9
6	"	"	1550	40	" "	$UO_{2.25}$	5,428	U_4O_9
7	"	"	1600	22	" "	$UO_{2.241}$	5,4307	U_4O_9
8	"	"	1700	15	" "	$UO_{2.227}$	5,429	U_4O_9
9	"	"	1850	300	" "	$UO_{2.227}$	5,432	U_4O_9
10	"	Tamman furnace with BeO tube	1400	60	" "	$UO_{2.235}$		
11	"	The same	1550	60	" "	$UO_{2.233}$	5,4272	$UO_{2.6}$-phase
12	"	Fused in electric arc in air	2700			$UO_{2.23}$ According to reduction: $UO_{2.237}$	5,437	$U_4O_9+UO_{2.6}$ / U_4O_9

*Using the terminology of Hoekstra and Siegel [1].

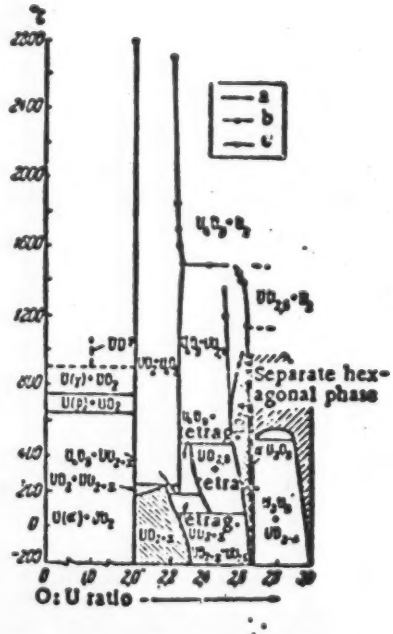

Fig. 4. Phase diagram of the U-O system. a) [2], b) authors of the present work, c) [6].

According to Akkermann [2], a two-phase region exists between UO_2 and U_4O_9 up to 1100° but Gronvold [3] discovered by high-temperature x-ray analysis that these oxides formed a continuous series of solid solutions above 900°. According to our data, samples with the compositions $UO_{2.62}$, $UO_{2.24}$ and $UO_{2.23}$, fired in a vacuum (10^{-3} mm Hg) furnace with a carbon tube at 1050, 1100 and 1600°, respectively, contained two phases and consisted of UO_2 and U_4O_9. However, the two phases we detected could have been formed by decomposition of a solid solution due to insufficiently rapid cooling.

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PHOSPHORYLATION OF CHLOROVINYL KETONES

PREPARATION OF PHOSPHORYLATED CHLOROVINYL KETONES FROM VINYL ACETATE AND ISOPROPENYL ACETATE

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(Presented by Academician A. N. Nesmeyanov, April 24, 1959)

In the present article we present the results from our study of the reaction of phosphorus pentachloride and the simplest enol acetates, namely, vinyl acetate and isopropenyl acetate; by means of this facile reaction we synthesized the first representatives of a new class of organophosphorus compounds – phosphorylated β-chlorovinyl ketones.

The interaction of isopropenyl acetate with phosphorus pentachloride may be represented in the following ways

$$CH_2C(OCOCH_3)=CH_2 + PCP_5 \rightarrow CH_3CCl(OCOCH_3)CH_2PCl_4 \xrightarrow{PCl_5} CH_3CCl_2CH_2PCl_4 + CH_3COCl + POCl_3.$$

The reaction did not stop at this stage. The acetyl chloride liberated smoothly acetylated the organophosphorus compound.

$$CH_3CCl_2CH_2PCl_4 + CH_3COCl \rightarrow CH_3CCl_2CH(COCH_3)PCl_4 + HCl$$

The PCl_4 group was converted into a $POCl_2$ group by the action of sulfur dioxide. We were unable to isolate the acid chloride of α-acetyl-β,β-dichloropropylphosphinic acid as it was unstable and lost hydrogen chloride partially during the reaction and completely on vacuum distillation to give the acid chloride of α-acetyl-β-chloropropenylphosphinic acid.

$$CH_3CCl_2CH(COCH_3)POCl_3 \xrightarrow{-HCl} CH_2C(COCH_3)=CPOCl_2.$$

However, the acid chloride of α-acetyl-β,β-dichloroethylphosphinic acid, obtained by the reaction of phosphorus pentachloride with vinyl acetate, was quite stable and did not lose hydrogen chloride during distillation. Under the reaction conditions we describe, the yield of the acid chloride of α-acetyl-β,β-dichloroethylphosphinic acid reached 85-90% and the yield of the acid chloride of α-acetyl-β-chloropropenylphosphinic acid was 70%.

The reaction equations presented show that two moles of phosphorus pentachloride should be used for each mole of enol acetate and of these, one mole is added to the double bond of the enol acetate and the second mole is consumed in replacing the acetoxy group by chlorine and forming acetyl chloride. Actually, if the reaction

was carried out with isopropenyl acetate and phosphorus pentachloride in a molar ratio of 1:1, the yield of phosphorylated β-chlorovinyl ketone did not exceed 40%. When two moles of phosphorus pentachloride were used in the reaction, the yield of the organophosphorus compound increased sharply. The acid chlorides synthesized were converted into phosphinic esters in the usual way with alcohol and pyridine. It should be noted that the application of this esterification method to the acid chloride of α-acetyl-β,β-dichloroethylphosphinic acid led to partial elimination of hydrogen chloride and did not give a pure compound. An analytically pure compound was obtained by esterification in the absence of base. The action of triethylamine on α-acetyl-β,β-dichloroethylphosphinic ester produced elimination of hydrogen chloride and formed α-acetyl-β-chlorovinylphosphinic ester in 88% yield.

We will use the new type of organophosphorus compounds obtained for various syntheses, characteristic of β-chlorovinyl ketones, and, first of all, for the preparation of phosphorylated heterocyclic compounds of the pyrazole, isoxazole and pyridine series.

EXPERIMENTAL

Preparation of acid chloride of α-acetyl-β,β-dichloroethylphosphinic acid. To a suspension of 125 g (0.6 mole) of phosphorus pentachloride in 150 ml of carbon tetrachloride was added 29.5 (0.3 mole) of freshly distilled vinyl acetate over a period of 45 minutes with stirring while the reaction mixture was kept at 15-17°. Stirring was continued for a further 2 hours, while the temperature of the bath was gradually raised to 40°. Sulfur dioxide was then passed (with water cooling) until the precipitate dissolved completely and the solvent, thionyl chloride and phosphorus oxychloride removed in vacuum at 30-35°. The residue was vacuum distilled.

We obtained 66 g (85% of theoretical) of the acid chloride of α-acetyl-β-β-dichloroethylphosphinic acid; b. p. 94-95°/2 mm; n_D^{20} 1.5100; d_4^{20} 1.5464; MR_D 49.88; calc. 49.47.

	Found	%:	C 18.44,	18.43;	H 2.11,	2.07;	P 12.04,	11.75;	Cl 54.80, 55.03
$C_4H_5O_2Cl_4P$	Calculated	%:	C 18.63;		H 1.98;		P 12.02;		Cl 54.88

Preparation of diethyl ester of α-acetyl-β,β-dichloroethylphosphinic acid. 1. In the absence of base. Over a period of ½ an hour, 18.4 g (0.4 mole) of absolute ethyl alcohol, diluted with 25 ml of ether, was added with stirring to a solution of 51.6 g (0.2 mole) of freshly distilled acid chloride of α-acetyl-β,β-dichloroethylphosphinic acid in 150 ml of ether. The reaction mixture was then heated for 2 hours on a water bath at 25-30°, flushed with air for 1 hour, and vacuum distilled.

We obtained 34.7 g (62.5% of theoretical) of the diethyl ester of α-acetyl-β,β-dichloroethylphosphinic acid. It had b. p. 111-112°/2 mm, n_D^{20} 1.4620; d_4^{20} 1.2465; MR_D 61.11; calc. 59.75.

	Found	%:	C 34.52;	34.87;	H 5.65;	5.71;	P 11.66;	11.21.	Cl 25.44; 25.37
$C_8H_{15}O_4Cl_2P$	Calculated	%:	C 34.67;		H 5.46;		P 11.18;		Cl 25.59

2. In the presence of pyridine. A mixture of 29.5 g (0.634 mole) of absolute ethyl alcohol and 50 g (0.634 mole) of pyridine was added dropwise to a solution of 81.7 g (0.317 mole) of the acid chloride in 200 ml of ethyl ether with stirring and cooling to −5-10°. On the following day the salt was removed and washed with ether, the solvent evaporated and the residue vacuum distilled. We obtained 45.6 g (52% of theoretical) of diethyl ester of α-acetyl-β,β-dichloroethylphosphinic acid with b. p. 111-112°/2 mm. Even after two or three distillations, the substance contained a small amount of the ester of α-acetyl-β-chlorovinylphosphinic acid.

Found %: C 35.72, 35.99; H 5.87, 6.04; P 11.67, 11.98.

Preparation of diethyl ester of α-acetyl-β-chlorovinylphosphinic acid. To a solution of 25.5 g (0.092 mole) of diethyl α-acetyl-β,β-dichlorophosphinate in 100 ml of benzene was added 9.3 g (0.092 mole) of triethylamine and the mixture heated under reflux for 2 hours. The salt formed was removed and washed with benzene; the benzene solution was washed once with 25-30 ml of a concentrated aqueous solution of sodium sulfate and dried over magnesium sulfate. After removal of the solvent, the residue was vacuum distilled. We obtained 19.45 g (88% of theoretical) of the diethyl ester of α-acetyl-β-chlorovinylphosphinic acid. It had b. p.

102-103°/2 mm; n_D^{20} 1.4645; d_4^{20} 1.1861; MR_D 56.83; calc. 54.42.

	Found %	C 30.49,	39.85;	H 6.09,	6.23;	P 13.20,	12.65;	Cl 14.79,	14.58
$C_5H_{10}O_4ClP$	Calculated %	C 30.03;		H 5.86;		P 12.87;		Cl 14.78	

Preparation of acid chloride of α-acetyl-β-chloropropenylphosphinic acid. With stirring, 20 g (0.2 mole) of freshly distilled isopropenyl acetate was added dropwise to a suspension of 83.2 g (0.4 mole) of phosphorus pentachloride in 100 ml of CCl_4. Stirring was continued for a further ½ hour while the bath temperature was gradually raised to 70-75°. On the following day sulfur dioxide was passed (with water cooling) until the precipitate dissolved completely. The solvent, thionyl chloride and phosphorus oxychloride were then removed in vacuum at 30-35°; the residue was distilled at 5 mm. After a small head fraction (3-4 g), the acid chloride of α-acetyl-β-chloropropenylphosphinic acid was collected; it had b. p. 120-127°/5 mm. The yield was 33 g (70% of theoretical). On redistillation, the substance boiled at 112-113°/1.5 mm and had n_D^{20} 1.5233; d_4^{20} 1.4413; MR_D 49.04; calc. 47.78.

	Found %	C 25.30;	25.14;	H 2.65,	2.64;	P 13.02,	13.22;	Cl 45.48;	45.48
$C_5H_6O_3Cl_2P$.	Calculated %	C 25.50;		H 2.57;		P 13.16;		Cl 45.18	

Preparation of diethyl ester of α-acetyl-β-chloropropenylphosphinic acid. A mixture of 55.7 g (0.68 mole) of pyridine and 32 g (0.68 mole) of absolute ethyl alcohol was added dropwise with stirring and cooling to a solution of 80 g (0.34 mole) of freshly distilled acid chloride of α-acetyl-β-chloropropenylphosphinic acid in 200 ml of ethyl ether. The salt formed was removed and washed with ether, the ether removed, and the residue vacuum distilled. We obtained 65.4 g (75% theoretical) of the diethyl ester of α-acetyl-β-chloropropenylphosphinic acid with b. p. 114-115°/1 mm, n_D^{20} 1.4710; d_4^{20} 1.1726; MR_D 60.70; calc. 59.04.

	Found %	C 42.46;	42.50;	H 6.61,	6.56;	P 12.03;	11.69;	Cl 13.03;	13.89
$C_9H_{16}O_4ClP$.	Calculated %	C 42.44;		H 6.33;		P 12.16;		Cl 13.92	

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SCANDIUM SELENIDE AND TELLURIDE

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The selenides and tellurides of rare-earth elements are of interest as semiconductors. Some of the properties of selenides of trivalent lanthanides and scandium, obtained from the anhydrous chlorides, are described in the literature [1]. There are no data on the crystal structure of the selenides of these elements. Only the tellurides of divalent cerium, europium, samarium, and ytterbium are known [2, 3, 4]. No tellurides of trivalent rare-earth elements have been described in the literature.

We synthesized scandium selenide and telluride from the elements. Metallic scandium was obtained by thermo-calcium reduction of anhydrous scandium chloride, synthesized by chlorination of spectrally pure scandium oxide with carbon at 1000° [5]. This scandium oxide contained less than 0.005% of impurity. It was prepared by thiocyanate extraction and precipitation of scandium oxalate [6]. "Rectifier grade" selenium, >99.99%, pure, was not purified further. High purity tellurium, >99.99 %, was obtained from technical tellurium containing ~6% of selenium, copper, lead and iron. The selenium was removed by two reprecipitations of tellurium dioxide, which lowered the content of it from 0.5% to >0.0002% [7]. Tellurium was separated from heavy metals

TABLE 1

X-ray Analysis of Scandium Selenide

Line No.	Intensity	hkl	d, kX found	d, kX calc.	a found, kX	Line No.	Intensity	hkl	d, kX found	d, kX calc.	a found, kX
1	4	111	3,118	3,121	5,400	10	2	333+511	1,040	1,040	5,405
2	5	200	2,701	2,702	5,401	11	3	440	0,9552	0,9557	5,403
3	5	220	1,910	1,911	5,401	12	2	531	0,9141	0,9137	5,408
4	5	311	1,629	1,630	5,400	13	5	600+442	0,9008	0,9008	5,405
5	5	222	1,560	1,560	5,405	14	5	620	0,8555	0,8546	5,410
6	2	400	1,352	1,351	5,408	15	1	533	0,8249	0,8244	5,409
7	2	331	1,240	1,240	5,405	16	5	622	0,8145	0,8149	5,403
8	5	420	1,209	1,209	5,405						
9	5	422	1,104	1,104	5,405						

$a_{av} = 5,405 \pm 0,005$ kX

after being reduced with sulfur dioxide by sublimation in high vacuum (10^{-4} - 10^{-5} mm Hg) at 400° [8].

For the synthesis of scandium selenide and telluride, samples of scandium and selenium (tellurium) of the order of 3-5 g, weighed with an accuracy of up to 0.0001 g, in an atomic ratio of 2:3, were carefully mixed and placed in quartz ampoules of ~10 ml volume, which were then evacuated to 10^{-4} - 10^{-5} mm Hg and sealed. Ampoules with a mixture of tellurium and scandium were heated in an electric furnace for 3 hours at 400°, then

the temperature was raised to 500° over 5 hours and subsequently to 1000° over 4 hours. The temperature conditions were changed somewhat in the synthesis of scandium selenide. The mixture was first held at 300° for 3 hours, then the temperature was raised to 500° over 5 hours and finally 1000° was reached over 5 hours. The scandium compounds were annealed at 1000° for 6 hours.

TABLE 2

X-ray Analysis of Scandium Telluride

Line No.	Intensity	hkl	d, kX found	d, kX calc.	a found, kX	Line No.	Intensity	hkl	d, kX found	d, kX calc.	a found, kX
1	1/8	*	3,580	—	—	15	4	422	1,184	1,185	5,801
2	3	111	3,360	3,352	5,810	16	4	333+511	1,117	1,117	5,805
3	5	200	2,900	2,902	5,818	17	2	440	1,027	1,027	5,805
4	1/8	*	2,613	—	—	18	5	531	0,9813	0,9813	5,805
5	1/8	*	2,347	—	—	19	5	600+442	0,9677	0,9675	5,806
6	1	$(333)_2$	2,230	—	—	20	5	620	0,9177	0,9179	5,803
7	5	220	2,056	2,053	5,813	21	2	533	0,8849	0,8853	5,802
8	1/8	$(620)_2$	1,835	—	—	22	4	622	0,8754	0,8752	5,806
9	4	311	1,750	1,750	5,805	23	3	$(1262)_2$	0,8592	—	—
10	4	222	1,676	1,676	5,805	24	3	444	0,8377	0,8379	5,803
11	1	$(640)_2$	1,612	—	—	25	4	711+551	0,8128	0,8128	5,805
12	2	400	1,451	1,451	5,805	26	4	640	0,8048	0,8050	5,803
13	3	331	1,330	1,331	5,801	27	4	642	0,7761	0,7757	5,808
14	4	420	1,296	1,293	5,794						

$a_{av} = 5,805 \pm 0,005$ kX

*Probably a stray impurity.

The scandium selenide and telluride were infusible crystalline powders: the former was brownish violet and the latter black. The compounds obtained were investigated by the x-ray powder method. The pictures were taken with a BSV electron tube with a copper anode and without filter. The intensity of the lines was estimated visually according to a scale of five. The x-ray pictures were measured on a comparator with reading accuracy of 0.05 mm. The results of the x-ray analysis are presented in Tables 1 and 2; the β-lines are not given.

TABLE 3

Values of Density and z for Scandium Telluride and Selenide

Compound	Density, g/cc		z	
	pyknometrically at 22°	x-ray	from pyknometric density	theoretical
Sc_2Te_3	5.26	5.32	1.32	$1\frac{1}{3}$
Sc_2Se_3	4.51	4.55	1.32	$1\frac{1}{3}$

All 16 lines of the scandium selenide picture were readily indexed for a face-centered cubic lattice with a = 5,[illegible]5 ± 0.005 kX (see Table 1). Of the 27 lines of the scandium telluride picture listed in Table 2, 20 lines were satisfactorily indexed for a face-centered cubic lattice with a = 5.805 ± 0.005 kX. If we consider lines No. 6, 8, 11, and 23 on the picture of Sc_2Te_3, then they are assigned the structurally possible indices $(333)_2$, $(620)_2$, $(640)_2$, and $(1262)_2$ in a double lattice with a = 11.61 ± ± 0.01 kX. The three unindexed weakest lines on picture of Sc_2Te_3 (Nos. 1, 4, and 5) cannot be ascribed to metallic scandium or tellurium and probably arise from stray impurities.

We determined the densities of scandium selenide and telluride at 22° pyknometrically with bromoform (see Table 3). The value obtained for the density of scandium selenide agrees well with literature data (4.52 g/cc [1]).

On the basis of the molecular weights of Sc_2Se_3 and Sc_2Te_3, the pyknometric densities and the lattice parameters, the number of formula units in the elementary cell of both compounds, z = $1\frac{1}{3}$ (see Table 3). Thus, the

crystal structure of both scandium selenide and telluride is of the type $\gamma' = Al_2O_3$ [9]. The structural defects concern scandium ions. With scandium telluride, lines No. 6, 8, 11, and 23 indicate partial transition of the structure $\gamma' = Al_2O_3$ into the structure $\gamma = Al_2O_3$ with a regular distribution of scandium ions.

Similar structures are found for indium telluride, In_2Te_3 [10], and also gallium selenide and telluride, Ga_2Se_3 and Ga_2Te_3 [11]; they can be considered as a type of sphalerite, but with defects with respect to the metal ions. The presence of the strong lines (200) with scandium selenide and telluride undoubtedly indicates that they are of structural type $\gamma = Al_2O_3$.

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DENSITY AND SETS OF ISOALKANES

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The possible number of lower isomeric alkanes was determined by Butlerov [1] and of the higher ones, in papers [2-6]. The first isoalkane, 2-methylpropane, was synthesized by Butlerov [1]. At the present time, all the C_4-C_{18} alkane isomers predicted by the theory of chemical structure have been synthesized. The number of C_{19}-C_{35} alkanes synthesized is small [7-10].

Depending on their structure, isoalkanes may have a higher or lower density than that of the n-alkanes with the same number of carbon atoms. Beginning with hydrocarbons with the composition C_7H_{16}, isomers with a greater density than that of the n-alkanes predominate among the isoalkanes. Thus, 5 of the 9 isomeric heptanes, 12 of the 18 isomeric octanes, 27 of the 35 nonane isomers and 64 of the 75 decane isomers have a greater density than that of the corresponding n-alkanes. A comparison of the densities of known alkanes shows that among them there are no two isomers of the same composition with absolutely identical densities but isomers similar in chemical structure may also have extremely similar densities, differing only in the fourth and fifth places. Since most branched alkanes with the composition $C_{22}H_{46}$ and above have not been synthesized and the synthesis of all possible isomers is a difficult problem practically, for the calculation of density is advantageous to choose from the great number of isomers only certain isoalkanes that interest us and then, if necessary, to synthesize them. The density of isomeric heptanes and octanes was calculated on the basis of molecular volumes of groups by Huggins [11] and the density of nonanes, decanes and undecanes was calculated by Francis [12] on the basis of density increments he deduced for isoalkanes of 9 types with different degrees of branching. Tatevskii [13] put forward a scheme for calculating the molecular volumes of alkanes on the basis of subtypes of bonds of the atoms forming the molecule, and so-called "constants" of effective volumes of these subtypes of bonds which made it possible to calculate the density of alkanes from the formulas for their chemical structure.

According to this scheme [13], the molecular volume of alkanes at 20° in ml/mole is $v_M = n_{13}A_{13}$ (41.47) + $+ n_{13}A_{13}$ (33.96) + $n_{14}A_{14}$ (30.00) + $n_{22}A_{22}$ (15.96) + $n_{23}A_{23}$ (6.65) + $n_{24}A_{24}$ (0.98) + $n_{33}A_{33}$ (−5.40) + $n_{34}A_{34}$ (−13.20)+ $+ n_{44}A_{44}$ (−22.90), where A represents the constants of effective volumes of subtypes of bonds and their values are given in brackets; $d^{20}_{calc} = (M/v^{20}_M)_{calc}$, where M is the molecular weight of the alkane; n is the number of the different subtypes of bonds in the alkane.

In comparison with other methods, this approximate calculation of the density of alkanes by Tatevskii's method [13] gives data which is more in agreement with experimental values. However, the so-called "constants" of the effective volumes of the bonds were calculated on the basis of experimental data referring predominantly to C_4-C_{11} alkanes and to a lesser extent to higher alkanes as less of them are known. Calculation of the density of higher isoalkanes of complex chemical structure according to the scheme in [13] smooths out the differences in the geometry of the molecules* and does not allow for the interaction of the atomic bonds. In connection

*The problem of the effect of rotation isomers on the density of alkanes requires further examination [6-19]. In particular, a calculation scheme was discussed at the conference on October 1, 1958 in the Institute of Organic Chemistry, Academy of Sciences USSR, in the report of V. M. Tatevskii, Yu. A. Pentin, E. G. Treshchov, and Kh. Keslerr "Potation isomerism and the energy of formation of hydrocarbons" [21].

with this, calculated data may differ somewhat from experimental values in the third and fourth places (even reaching 0.015 sometimes) and evidently, in order to obtain more accurate results, some refinement is needed of the so-called "constants" of the effective volumes of the bonds, especially for calculating the density of C_{20}-C_{30} isoalkanes. Thus, according to our data, when the "constant" $A_{22} = 15.98$ was used in Tatevskii's scheme to calculate the density of trialkylmethanes with the composition $C_{21}H_{44}$-$C_{31}H_{76}$ synthesized by Challenger and Pantony [15], data were obtained which differ from the experimental values by 0.0167 and when $A_{22} = 16.3$, which we calculated from experimental data on the properties of alkanes with the composition $C_{19}H_{22}$-$C_{16}H_{34}$, the difference was only 0.0032. On the basis of experimental data [7-10], data calculated by Francis [12] and data from our calculations by Tatevskii's method [13], we constructed a graph (see Fig. 1) of the increase in the density of alkanes with the composition C_6-C_{20}, where the density of n-alkanes is plotted on curve 1, the minimal density of isoalkanes on curve 2, and the maximal density of isoalkanes on curve 3.

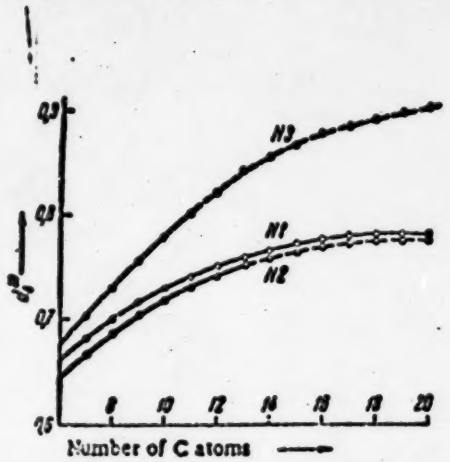


Fig. 1. Density of alkanes with the composition C_6H_{14}-$C_{20}H_{42}$. 1) Density of n-alkanes; 2) minimum density of isoalkanes (C_6-C_{13} experimental data, C_{14}-C_{20} calculated); 3) maximum density of isoalkanes (C_6-C_{11} experimental data, C_{12}-C_{20} calculated).

From these data it follows that the following, for example, have a lower density than that of the corresponding n-alkanes: 2,4-dimethylpentane – d_4^{20} 0.6727, 2,2,4-trimethylpentane – d_4^{20} 0.6919; 2,2,5-trimethylhexane – d_4^{20} 0.7071; 2,2,5,5-tetramethylhexane – d_4^{20} 0.7183; 2,2,4,6-tetramethylheptane – d_4^{20} 0.7335; 2,6-dimethyl-4-propylheptane – d_4^{20} 0.7443; 2,5,9-trimethyldecane – d_4^{20} 0.7546; 2,2,13,13-tetramethyltetradecane – d_4^{4} 0.7742 (calculated) and certain other isomers (see Fig. 1, Curve 2). The maximum density is possessed by 3-ethylpentane – d_4^{20} 0.6932, among the heptanes; 3-methyl-3-ethylpentane d_4^{20} 0.7274, among the octanes; 2,2,3,3-tetramethylpentane d_4^{20} 0.7567, among the nonanes; 3,3,4,4-tetramethylhexane – d_4^{20} 0.7824; among the decanes and 3,3,4-trimethyl-4-ethylhexane – d_4^{20} 0.7978, among the undecanes. Our calculated data show that among the isoalkanes with the composition $C_{12}H_{26}$, the hydrocarbon with the highest density has a density of 0.8246, with the composition $C_{13}H_{28}$, a density of 0.8420; $C_{14}H_{30}$ – a density of 0.8576; $C_{15}H_{32}$ – d_4^{20} 0.8718; $C_{16}H_{34}$ – d_4^{20} 0.8844; $C_{20}H_{42}$ – a density of ≈ 0.9 (see Fig. 1, Curve 3) and for $C_{35}H_{74}$, isoalkanes with a density ≈ 1.0 may exist.

Isoalkanes of the type $R\left(-\underset{R}{\overset{R}{\underset{|}{\overset{|}{C}}}}\right)_n-R$ and $R'-\underset{R}{\overset{H}{\underset{|}{\overset{|}{C}}}}\left(-\underset{R}{\overset{R}{\underset{|}{\overset{|}{C}}}}-\right)_n-\underset{R}{\overset{H}{\underset{|}{\overset{|}{C}}}}-R'$

have the highest density. An examination of the possibilities of constructing isoalkane molecules from a given number of atoms and number of different subtypes of bonds of these atoms shows that, on the basis of only the number of subtypes of atomic bonds, it is not possible in all cases to determine unequivocally the chemical structure of the alkane molecule as in principle two cases for the construction of the molecules are possible: 1) with a given number of subtypes of atomic bonds, it is possible to construct only one isomer and 2) with a given number of bond subtypes it is possible to contruct several isomers. Thus, each alkane with the composition of C_4H_{10}-C_7H_{16} may be characterized by a definite number of different bond subtypes of the given class of hydrocarbons, i.e., with a given number of different bond subtypes, just this one isomer is possible. However, beginning with C_8H_{18}, with the same number of bond subtypes it becomes possible to form not one, but several isoalkanes, in particular, two isooctanes: 3- and 4-methylheptanes with d_4^{20} 0.7058 and d_4^{20} 0.7046 (0.7046 calc.); three methylnonanes: 3-, 4-, and 5-methylnonanes with d_4^{20} 0.7335, 0.7323, 0.7325 (0.7332 calc.); two (3,4- and 4,5-) dimethyloctanes; two (3,3- and 4,4-) dimethyloctanes; two isodecanes: 3,3,4,4-tetramethylhexane with d_4^{20} 0.7824 [10] and 2,2,3-trimethyl-3-ethylpentane with d_4^{20} 0.7818 (14), (0.78178 calc.) etc. We have called such groups of isoalkanes, which have the same number of different subtypes of atomic bonds but different chemical structures,

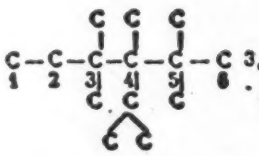
sets of isoalkanes. As stated above, each member of a set of isoalkanes has the same number of different bond subtypes and by calculating the density of one of them we will know the approximate density of any other member of this set with an accuracy to the third place. As the molecular weight increases, the number of sets grows and with an increase in the degree of branching of the alkane molecule, the density of each isomer gradually increases, reaching the possible maximum. In contrast to the lower alkanes C_7H_{16}-C_9H_{18}, where there are single isomers with the maximal density, among the higher ones, the existence of sets of alkanes with maximal and very close to maximal density is possible.

Among the isomers of tetradecane there is a set with the maximal density of 0.8576, consisting of two members: 2,2,3,3,4,4,5,5-octomethylhexane and 2,2,3,4,4-pentamethyl-3-tert.-butylpentane, a set with a density of 0.8574.

Let us consider the method of finding the members of a set with a given density. Let us take $C_{14}H_{30}$

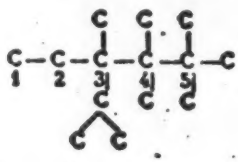
2,2,4,4-tetramethyl-3-ethyl-3-isopropylpentane (I)

which has a density of 0.8574, calculated on the basis of the number of bond subtypes in the given isoalkanes A_{12} = 1; A_{13} = 2; A_{14} = 6; A_{22} = 0; A_{23} = 0; A_{24} = 1; A_{34} = 1; A_{44} = 2. Without changing the number of different subtypes of bonds indicated, but by changing the order of attachment of the groups in the molecule by the interchange of radicals, for example, in order of precedence, we obtain isoalkanes of different chemical structure – new members of the set. Thus, by exchange of the methyl group at the 2nd carbon atom (methol-2-) with the ethyl group (ethyl-3-) we obtain from I



3,3,4,5,5,-pentamethyl-4-isopropylhexane. (II)

By exchange of methyl-3 with isopropyl-4, from II we obtain



3,4,4,5,5-pentamethyl-4-isopropylhexane. (III)

By exchange of methyl-5 with isopropyl-3, from III we obtain

3,3,4,4,5,5,6-heptamethylheptane. (IV)

Obviously, the members of the set can be found similarly, beginning with IV, III or II.

Among the isopentadecanes there is a set with the maximal density of 0.8718, consisting of four members and one with a density of slightly less than 0.8704, also consisting of four members, there is also a set with a density of 0.8453, consisting of six isomers: 2,2,4,4,5,5- hexamethyl-3-ethylheptane, 3,3,4,5,5,6,6-heptamethyloctane

etc.; the set of isohexadecanes with the maximal density of 0.8844 consists of five members, and that with a density of 0.8740 also consists of five members. The number of members of sets of isoalkanes with the maximal density and close to it increases gradually with an increase in the molecular weight and for hexatriacontane there can exist sets of isoalkanes with a density of ~1.0 (±0.01), consisting of 78 and more members.

This possibility of the existence of sets of isoalkanes, especially those with maximal density and sets close to this, makes it possible, from a consideration of the structural formulas of all the members of a family of isoalkanes, to choose from them the hydrocarbon whose synthesis involves least difficulties from steric hindrance and the phenomena of isomerization and dissociation of the starting compounds. The idea of sets may also be used in characterizing other classes of hydrocarbons, in particular, the higher isoalkenes, acetylenic hydrocarbons, and certain other classes. After becoming acquainted with our work, V. M. Tatevskii [20] began investigations to determine the number of sets of isoalkanes.

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HETEROGENEOUS CATALYTIC COURSE OF BENZENE PYROLYSIS

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When benzene vapor is heated above 500-600° in the presence of the most varied catalysts, dehydrocondensation reactions occur and the main one of these is diphenyl formation:

$$2C_6H_6 = C_6H_5 \cdot C_6H_5 + H_2.$$

Beginning with Berthelot [1], many investigators have studied the synthesis of diphenyl by the pyrolysis of benzene, though until now no light has been shed on the role of catalytic surfaces in the pyrolysis. The opinion is held that all pyrolysis reactions are non-catalytic and purely thermal [2, 3] and that this includes the dehydrocondensation of benzene [4-6]. The basis of this opinion is the hypotheses (far from proved) on the indifference of the nature of the catalyst for benzene pyrolysis reactions and the fact that the reactions themselves are homogeneous. On the other hand, a series of authors consider that the dehydrocondensation of benzene is a heterogeneous catalytic reaction [7-10], without presenting specific evidence. This is supported by the fact that different known catalysts are used in the pyrolytic preparation of diphenyl from benzene and by the search for better catalysts, as shown by the large patent literature.

In this work we studied the role of the catalyst surface in the pyrolysis reactions of benzene, especially the formation of diphenyl, and the specificity of catalysts of different natures.

The work was carried out in a flow apparatus for heterogeneous catalytic investigations with a detachable quartz reactor [11] by the procedure we developed [12]. The volume of the catalyst was 5 ml. The volume rate of benzene input was 1.0 hour^{-1}. The experiments were at atmospheric pressure. The carbon was allowed for by weighing the reactor on analytical balances. The diphenyl was estimated after evaporation of the benzene from the quantitatively collected catalyzate.

Carbon formation during benzene pyrolysis is undoubtedly a heterogeneous process since the carbon is formed as a film on the walls of the apparatus and on the surface of the catalyst mass. The differences in opinions with respect to the heterogeneity or homogeneity of benzene pyrolysis reactions apparently only refer to the reactions by which diphenyl and other volatile products are formed.

In our experiments, increasing the surface of the catalyst had a positive effect, which may be considered to show the heterogeneous catalytic character of the reaction, for if it were homogeneous there would not be any effect. However, the specific catalytic activity of the catalyst did not remain constant. As follows from Table 1, an increase in the catalyst surface by 70 and 220% led to a considerably smaller increase in the reaction rate at temperatures below 825°. With an increase in temperature from 700 to 825°, a gradual increase in the reaction rate was observed and at 825° the increase in rate corresponded to the increase in the catalyst surface, i.e., under these conditions the surface of silica glass has a constant specific catalytic activity.

To study the specificity of different catalysts in the pyrolysis reactions, we investigated a series of deposited catalysts: metal-silica gel (see Table 2). Approximately identical molar amounts of different metals (0.5-6 weight %) were deposited on ASK silica gel by impregnation with a solution of the nitrate with subsequent decomposition and reduction.

TABLE 1

Effect of Specific Surface of Catalyst on the Reaction Rate of Diphenyl Formation in Benzene Pyrolysis

Experimental conditions	Catalyst surface cm^2*	Increase in surface in comparison with empty reactor, %	Increase in reaction rate in comparison with an empty reactor with the same contact time, %					
			at 700°	at 730°	at 750°	at 775°	at 800°	at 825°
Empty silica glass reactor	247	0	0	0	0	0	0	0
Reactor with silica glass filling	432	70	15	15	10	11	27	65
Reactor with silica glass filling	797	220	76	46	46	57	117	220

*The surface was determined by geometrical calculation. The value of the surface also included the catalyst tube surface which was at the experimental temperature.

The catalysts had similar surfaces (according to benzene adsorption at 0°, the specific surface was ~100 m^2), i.e., the observed differences in specificity may be assigned wholly to differences in the natures of the deposited metals.

As follows from Figs. 1 and 2, clear differences exist in the specificity of the catalysts investigated. Iron on silica gel shows a greater catalytic activity in diphenyl formation than Ni and Co (see Fig. 1). In their turn,

TABLE 2

Composition of Catalysts and Ratio of Rates of Diphenyl and Carbon Formation in Benzene Pyrolysis

Catalyst	Metal content, g-at.	Ratio of rates of diphenyl and carbon formation				
		at 650°	at 700°	at 750°	at 800°	at 850°
Silica gel	—	19,2	17,3	9,8	4,7	3,8
Fe on silica gel	$2,4 \cdot 10^{-4}$	2,3	2,5	2,3	1,8	1,3
Ni on silica gel	$2,3 \cdot 10^{-4}$	1,5	5,0	4,1	3,5	1,8
Co on silica gel	$2,75 \cdot 10^{-4}$	5,3	5,8	7,2	3,6	2,6
Cu on silica gel	$2,06 \cdot 10^{-4}$	7,1	7,0	5,1	3,9	1,9
Ag on silica gel	$1,65 \cdot 10^{-4}$	36,0	8,2	4,4	3,8	6,3
V_2O_5 on silica gel	$2,11 \cdot 10^{-4}$	12,7	10,5	8,3	4,0	2,1
	$0,31 \cdot 10^{-4}$	1,2	1,3	1,9	2,8	4,0

the last two catalysts behave almost identically and are very similar to Cu on silica gel. V_2O_5 on silica gel is even less active in diphenyl formation than Cu, Ni, and Co, but is more active in carbon formation (see Fig. 2). Ag, Fe, and V_2O_5 on silica gel cause maximum carbon formation at 800°, while this maximum is absent with other catalysts, etc.

Besides the difference in comparative value of the catalytic activity in the processes of diphenyl and carbon formation, the results obtained indicate the existence of very sharp differences in the rates of the two main benzene pyrolysis reactions (diphenyl and carbon formation) on different catalysts. The value of this ratio may be considered as a definite measure of the specificity of the catalyst for one or the other of the processes.

As follows from Table 2, each catalyst is characterized by a definite course for the change in this value with an increase in temperature, which is also characteristic of the specificity. Thus, in the case of iron, nickel, and cobalt catalysts, maxima were observed in this value at certain temperatures; in the case of Cu and Au, the value fell sharply with an increase in temperature; in the case of Ag there was a minimum at 800°; on the contrary, in the case of V_2O_5, an increase in the ratio was observed with an increase in temperature.

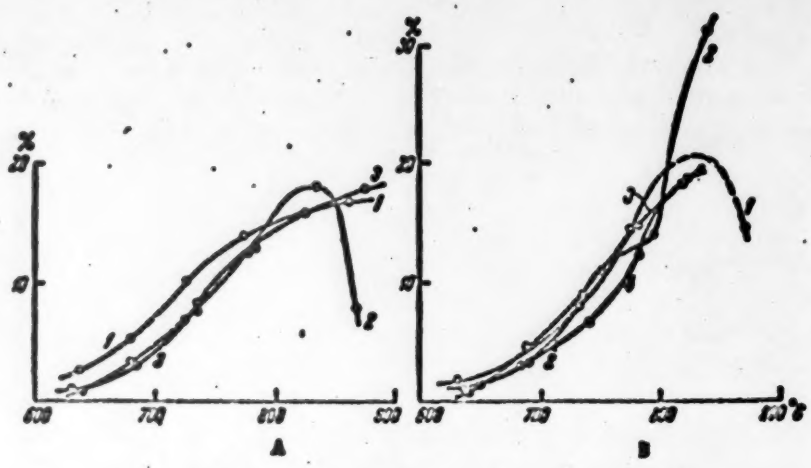

Fig. 1. Temperature dependence of crude diphenyl yields in benzene pyrolysis on catalysts on silica gel: A) Fe (1), Ni (2), Co (3); B) Cu (1), Ag (2), Au (3), V_2O_5 (4).

On the basis of these data it must be admitted that the nature of the catalyst is by no means as indifferent as is sometimes accepted [4, 5] and clearly detectable peculiarities can be discerned in the specificity of the catalysts and in their catalytic activity with respect to the separate reactions of benzene dehydrocondensation. The specificity of the catalysts also indicates a heterogeneous catalytic mechanism for benzene pyrolysis.

In connection with this problem, we should note certain interesting facts on physical changes in the surface of the catalysts which occur only in the sphere of the reaction and are not observed during simple heating of the catalyst in an inert medium (nitrogen).

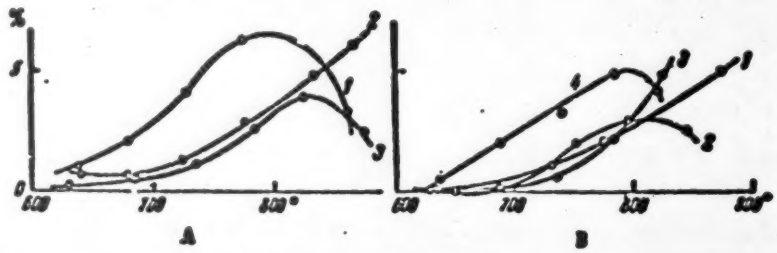

Fig. 2. Temperature dependence of carbon yields in benzene pyrolysis on catalysts on silica gel: A) Fe (1), Ni (2), Co (3), B) Cu (1), Ag (2), Au (3), V_2O_5 (4).

During experiments at 500-800°, on participating in the pyrolysis reactions of benzene (up to 20% of diphenyl was formed and no carbon), the grains of a copper catalyst underwent more or less strong "welding" at their point of contact with each other and the strength of the "welding" was greater the higher the experimental temperature and the closer the grains to the front part of the catalyst bed (the temperature was the same throughout the bed). There was no "welding" in analogous experiments in an inert medium of nitrogen. As followed

from microscopic investigations, the "welding of copper grains occurred as a result of recrystallization, i.e., under the conditions of benzene dehydrocondensation, copper atoms migrated along the surface of the catalyst.

From the appearance of sections with micro-cracking and optical anisotropy, we observed microscopically the recrystallization of amorphous silica glass as a result of its participation in the pyrolysis of benzene at 700-750°. When the glass was heated at 730° in the reaction sphere for 12 hours, complete recrystallization of the surface occurred. Simple heating of silica glass in an atmosphere of nitrogen at the same and a higher temperature did not lead to any changes. In this case, the recrystallization evidently was also connected with the migration of atoms or groups of atoms on the glass surface. In the opinion of Balandin [14], the migration of catalyst atoms must consist of the transfer of a whole multiplet complex, which also includes the atoms of the active center, from one place to another with its subsequent decomposition in the new place. The migration of catalyst atoms as a result of the thermal motion of catalytic complexes is more favored energetically than their movement from natural thermal motion (the energy of removal of a multiplet complex from the lattice, $\lambda_{a-k,k}$, is considerably less than the heat of sublimation of the catalyst, λ_k).

The fact that we observed recrystallization of the catalysts only in the reaction zone of benzene pyrolysis and did not observe it when the catalysts were heated in an inert gas can only be explained from the point of view presented. It can be assumed that due to the heterogeneous catalytic character of diphenyl formation, the migration of atoms and groups of atoms of the catalyst is facilitated due to the formation of catalytic complexes.

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DEPENDENCE OF THE HYDROGENOLYSIS OF ORGANOSULFUR COMPOUNDS ON THEIR STRUCTURE

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(Presented by Academician A. A. Balandin, May 6, 1959)

After the classical work of S. V. Lebedev and his co-workers [1, 2, 3], selective hydrogenation found wide application both as a method of establishing the structures of unsaturated hydrocarbons and as a method of analyzing multicomponent mixtures of ethylenic hydrocarbons.

In recent years, in petroleum chemistry, the study of the structure, properties and reactions of organosulfur compounds, which are present in considerable amounts in medium and high-molecular fractions of petroleum, has acquired great practical value. In this connection, communications have begun to appear in the literature quite frequently on the application of catalytic hydrogenation to the solution of the structure of organosulfur compounds [4]. Raney nickel is used most frequently in these cases. In our previous work [5] it was shown that the desulfurization of organosulfur compounds proceeds smoothly in the presence of such a catalyst as a mixture of tungsten and nickel sulfides deposited on aluminum oxide. This catalyst is used for destructive hydrogenation at high temperatures, while at temperatures of 250-270° it promotes selective hydrogenation, directing the attack of hydrogen to C-S bonds. It seemed interesting to use the high selectivity of this catalyst for developing a method of group analysis of organosulfur compounds present in medium and higher petroleum fractions. The first and main step in solving this problem was a study of the desulfurization rates of individual synthetic organosulfur compounds of various structures under mild, selective catalytic hydrogenation conditions.

To solve this problem we used 8 individual organosulfur compounds. By the example of some of these compounds, we showed previously [6] that they were desulfurized at very different rates in the presence of Raney nickel at 60° and this was caused by the difference in the bond strengths. The use of a more selective catalyst such as a mixture of nickel and tungsten sulfides deposited on aluminum oxide, made it possible to obtain an even more clearly expressed difference in the desulfurization rates of individual organosulfur compounds of different structures.

This catalyst has a series of essential advantages over Raney nickel, namely, it is extremely stable to long storage, is insensitive to poisoning by sulfur, has a high selectivity and stability during operation and, finally, is an industrial catalyst. In hydrogenation experiments we used a catalyst with a grain size of 1-1.5 mm. A constant weight ratio of catalyst : sulfur of 2 : 1 was maintained in all experiments.

The catalytic hydrogenation experiments were carried out in a rotating autoclave with a capacity of 0.5 liter and at a temperature of 200° and a working hydrogen pressure of 200 atm. The organosulfur compounds were loaded into the autoclave as a solution in cetane (0.5 mole/liter of cetane). The course of the process was followed by the change in the sulfur content of the liquid phase.

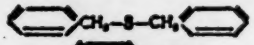
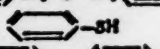
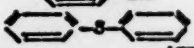
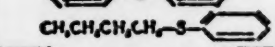
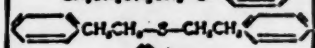
As was shown in a previous investigation [7], the phenomena of isomerization and cracking of the benzene ring were not observed in the presence of a nickel-tungsten sulfide catalyst at temperatures below 250°.

Thus, the temperature region we chose guaranteed a desulfurization reaction under conditions that practically excluded side and secondary processes.

From the data presented in Table 1 and Fig. 1, it is evident that the organosulfur compounds we investigated clearly fitted into three groups with respect to the elimination of sulfur under selective, catalytic hydrogenation conditions.

TABLE 1*

Rate of Hydrogenolysis of Organosulfur Compounds (220°, 200 atm)

Sulfur compounds	Structural formula	Desulfurized, in %, after time, in hours									
		1	2	3	4	6	8	10	12	14	16
Dibenzyl sulfide		89	100								
Thiophenol		30	73	100							
Diphenyl sulfide		—	25	—	52	71	92	100			
n-Butyl phenyl sulfide		—	10	—	26	50	58	70	83	09	100
Diethyldiphenyl sulfide		—	14	—	30	42	—	58	72	83	99
Benzthiophene		—	—	—	16	—	33	—	45	—	59**
Dibenzthiophene		Not desulfurized									
Tetraphenylthiophene		Not desulfurized									

* Diethyldiphenyl sulfide and dibenzyl sulfide were synthesized by S. D. Pustil'nikova. Z. K. Zemskova and P. V. Ratnikova participated in the analytical part of the work.

** 73, 86, and 96%, respectively, after 20, 24, and 28 hours.

Dibenzyl sulfide and thiophenol belong to the first group of the most readily desulfurized compounds. In this case, the sulfur was removed completely after 2-3 hours.

The second group consisted of aromatic and mixed alkyl aromatic sulfides, which required 14-16 hours for complete desulfurization. We should emphasize the presence of a noticeable difference in the rates of desulfurization of this group of compounds.

The third group consisted of tetrasubstituted thiophenes (dibenzthiophene and tetraphenyl thiophene), which were quite stable under the conditions of our experiments (220° and 200 atm of hydrogen). Desulfurization of dibenzthiophene became noticeable only at 250° and tetraphenylthiophene was even more stable. A disubstituted thiophene (benzthiophene) occupied an intermediate position between the second and third groups.

If we take the time for 50% desulfurization of dibenzyl sulfide as unity, then we obtain the following (Table 2) values for all the organosulfur compounds investigated and these characterize the relative rates of their desulfurization.

A comparison of these data shows that a phenyl group in a position α to a sulfur atom in a carbon chain very considerably reduces the strength of the C-S bond, while moving this group to a position β to the sulfur atom almost completely eliminates its effect on the strength of the C-S bond in the chain. The strength of a C-S bond in a

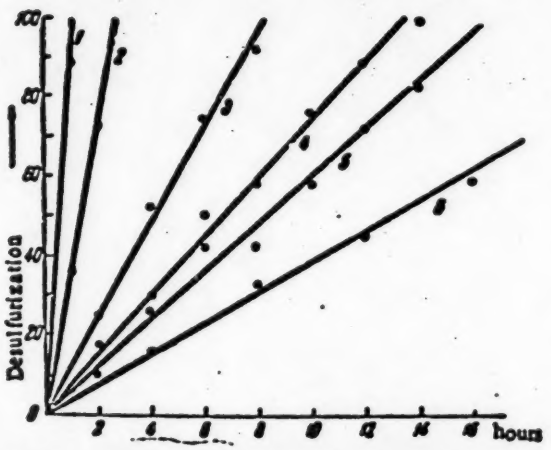


Fig. 1. Rates of hydrogenolysis of sulfur compounds. 1) Dibenzyl sulfide, 2) thiophenol, 3) diphenyl sulfide, 4) n-butyl phenyl sulfide, 5) diethyldiphenyl sulfide, 6) benzthiophene.

TABLE 2

Relative Rates of Desulfurization of Organosulfur Compounds

Organosulfur compound	Relative rate of hydrogenolysis	Organosulfur compound	Relative rate of hydrogenolysis
Dibenzyl sulfide	1	n-Butyl phenyl sulfide	11
Thiophenol	2.5	Diethyldiphenyl sulfide	15
Diphenyl sulfide	7	Benzthiophene	25

thiophene ring is much greater than in an aliphatic chain. At the present time, we are elucidating the effect of the degree of substitution of the thiophene ring and the nature of the substituents on the strength of the C-S bond.

The amount of aromatic hydrocarbons (benzene, toluene and ethylbenzene, respectively), which must be formed on removal of the sulfur atom from the organosulfur compound, was determined in the reaction products. In all cases about 90% of the corresponding hydrocarbon was found.

Among the hydrogenation products, 6.7% of mercaptan was found in the case of n-butyl phenyl sulfide and 0.9% in the case of benzthiophene.* This is direct experimental proof that the desulfurization proceeds as a two-stage process with the intermediate formation of a mercaptan, $C_6H_5SC_4H_9 \rightarrow C_6H_5SH + C_4H_{10}$.

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*The mercaptans were determined by potentiometric titration by the procedure developed by I. A. Rubinshtein and Z. A. Kleimenova.

** In Russian

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SPECTROPHOTOMETRIC INVESTIGATION OF PICRATES OF AROMATIC HYDROCARBONS IN SOLUTION

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Chemical Institute, Kazan Branch of the Academy of Sciences USSR
(Presented by Academician B. A. Arbuzov, April 27, 1959)

A characteristic of a large group of aromatic compounds is their tendency to interact with polynitro derivatives of benzene and phenol and, in particular, picric acid [1]. The picrates of naphthalene and anthracene and their homologs are molecular compounds which crystallize readily and melt at a strictly defined temperature and they have often been prepared for the identification and isolation of the corresponding hydrocarbons. The picrates of benzene and its lower homologs could not have been crystallized [2].

Almost all aromatic hydrocarbons are transparent to visible light; their absorption bands are in the ultraviolet region [3]. Crystalline picrates have a characteristic color, which is deeper than that of pure picric acid, and its intensity increases with the complexity of the hydrocarbon molecule [4].

In this connection, the question arises as to whether aromatic hydrocarbons can be characterized by the light absorption of their picrates. This could be useful especially in the investigation of suitable fractions of petroleum and petroleum products. On the other hand, a systematic investigation of the absorption spectra of picrates could provide additional data on the physicochemical nature of complex-formation between aromatic compounds and polynitro derivatives of benzene.

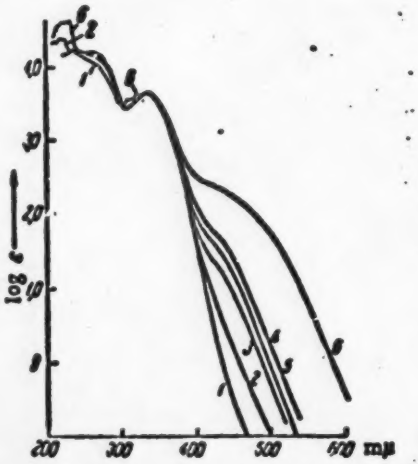

Fig. 1. Absorption spectra of dichloroethane solutions of picric acid (1) and naphthalene picrate (2 – 0.01 M; 3 – 0.05 M; 4 – 0.1 M; 5 – 0.2 M); 6-0.1 M 2,3,6-trimethylnaphthalene picrate.

The solvent we used was 1,2-dichloroethane, which quite readily dissolves both picric acid and hydrocarbons as well as their picrates.

Due to partial dissociation on solution of naphthalene picrate in dichloroethane, an equilibrium is set up between the picrate and its components, namely, naphthalene and picric acid. However, in such a case an identical result must be obtained by dissolving the picrate and by directly dissolving picric acid and naphthalene, taken in stoichiometric amounts. Experiment confirmed our hypothesis and, subsequently, in investigating the absorption spectra of various hydrocarbons it was not necessary to have isolated, crystalline picrates. This not only simplified the working procedure but also extended the scope of the investigation to hydrocarbons whose crystalline picrates are unknown.

By the isomolar series method [5], we obtained certain data, characterizing the complex formed by naphthalene with picric acid in dichloroethane. It was found that as in the crystalline picrate, the components formed a complex with a 1:1 molecular ratio in solution.

Since the degree of dissociation of the complexes increased with dilution of the solution, most investigations were made with quite concentrated solutions (0.1 and even 0.2 M). They were prepared by adding samples of pure hydrocarbons, weighed on microbalances, to appropriate standard 0.1 or 0.2 M solutions of picric acid in dichloroethane. We plotted the absorption curves over quite a wide spectral range* and calculated the molar extinction ϵ for a series of solutions (Fig. 1). While the molar extinction did not depend on dilution for solutions of pure picric acid, the form of the curves was different concentrations in the case of solutions containing an equimolar amount of naphthalene in addition to picric acid.

The absorption spectra of the solutions investigated may be separated into three parts. In the shortest-wave section of them (222-300 mμ), absorption bands characteristic of naphthalene hydrocarbons appear.

The absorption maximum of picric acid (340 mμ) appeared in the middle part. Here the molar extinction curves were the same for solutions of different concentrations and containing different hydrocarbons. Together with the absorption spectra of naphthalene solutions, Fig. 1 shows the curve for a 0.1 M solution of 2,3,6-trimethylnaphthalene. The curves coincide completely over the region considered. The absorption is caused by picric acid here and its value remains unchanged regardless of whether the acid is free or bound in a complex. This fact was used for developing a spectrophotometric method of determining the molecular weight of picrates [6].

The longwave part of the spectrum characterizes the absorption of the picrates themselves. The higher the concentration of the latter, the lower is the wavelength at which the absorption curve begins to branch out from the picric acid curve. The greatest difference in the course of the curves is shown in the wavelength region above 400 mμ, where the concentration dependence of the extinction is seen most sharply.

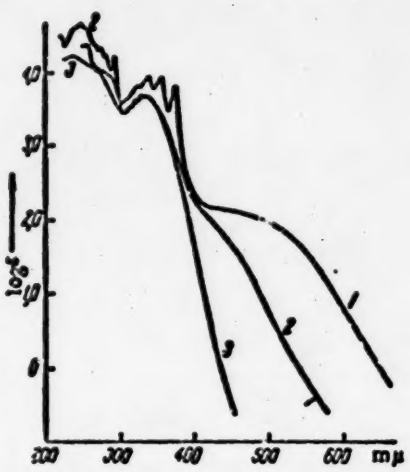

Fig. 2. 1) Absorption spectra of 0.1 M dichloroethane solutions of anthracene picrate; 2) of phenanthrene picrate; 3) picric acid curve.

This result confirmed our opinion on the advantage of investigating picrates of aromatic hydrocarbons in the visible region of the spectrum and proved the possibility of using the steeply falling edge of the absorption band for analytical purposes. The character of the displacement of absorption band edge was the same under the effect of a change in concentration and as a result of a change from one hydrocarbon to another. However, for solutions of a definite concentration the displacement of the absorption band quite unequivocally characterized the hydrocarbon forming the complex with picric acid.

Together with naphthalene and its methyl derivatives, certain non-condensed aromatic hydrocarbons were investigated. We also took an aliphatic hydrocarbon, n-heptane, but here the absorption curve did not differ from that of pure picric acid. It was not displaced either when a mixture of solid paraffins was added to the solution.

For all the solutions investigated, the edges of the absorption bands in the visible part of the spectrum were almost parallel to each other and the separation between the curves measured at a definite optical density, for example, at D = 1, may be taken as a measure of the displacement of the edge. Appropriate data are given in Table 1. The investigation was carried out on an SF-4 spectrophotometer at room temperature. All the substances used were purified and their constants compared with literature data. The purity of the series of preparations was established by plotting the Raman spectra and the ultraviolet absorption spectra.

The great difference between the displacement of the absorption band for picrates of naphthalene and its derivatives and the corresponding values for benzene and its homologs is very noticeable. With an increase in the number of alkyl groups, the value of $\Delta\lambda$ increases, as can be seen on the example of benzene, toluene, the xylenes, and mesitylene. The same is observed for naphthalene derivatives.

* Due to the great differences in absorption in different regions of the spectrum, cells with layer thickness from 0.05 to 100 mm were used.

Two interesting peculiarities should be noted. The first of these is that the position of the alkyl groups in the ring has little effect on the value of $\Delta\lambda$. The latter is the same for o- and m-xylenes, α- and β-methylnaphthalenes, and 2,3- and 2,6-dimethylnaphthalenes and differs only slightly for mesitylene and pseudocumene.

The second peculiarity is the fact that the value of $\Delta\lambda$ hardly changes when the alkyl groups become more complex. Thus, they are very similar for toluene, ethylbenzene, and isopropylbenzene (cumene) and for the xylenes and cymene. At the same time, the introduction of new methyl groups into the ring considerably increases

TABLE 1

Displacement of the Edge of the Picric Acid Absorption Band ($\Delta\lambda$) at an Optical Density of D = 1 under the Effect of Equimolecular Amounts of Hydrocarbons

	0.1 M solutions		0.2 M solutions			0.1 M solutions		0.2 M solutions	
	$\lambda_{D=1}$ mμ	Δλ	$\lambda_{D=1}$ mμ	Δλ		$\lambda_{D=1}$, mμ	Δλ	$\lambda_{D=1}$, mμ	Δλ
Solutions without hydrocarbons	412	—	419	—	α-Methylnaphthalene	480	68	509	90
Benzene	412	0	421	2	β-Methylnaphthalene	480	68	509	90
Toluene	413	1	423	4	2,3-Dimethylnaphthalene	503	93	—	—
Ethylbenzene	413	1	—	—	2,6-Dimethylnaphthalene	503	93	537	118
Cumene	414	2	—	—	2,3,6-Trimethylnaphthalene	537	125	—	—
o-Xylene	416	4	428	9	1,2,3,6-Tetrame.-naphthalene	577	165	—	—
m-Xylene	416	4	428	9	Acenaphthene	526	114	—	—
p-Cymene	417	5	431	12	Phenanthrene	483	78	—	—
Diphenyl	420	8	—	—	Anthracene	590	178	—	—
Mesitylene	424	12	442	23	Decalin	414	2	—	—
Pseudocumene	429	17	451	32					
Tetralin	423	11	437	18					
Naphthalene	455	43	481	62					

the absorption. For naphthalene derivatives, a dependence close to linear is observed between the number of methyl groups and the value of the displacement in the edge of the absorption band. These observations may be useful in determining the structure of hydrocarbons.

The displacement of the absorption band in the case of decalin is extremely small and the absorption of tetralin picrate is of a similar order to the values for derivatives of benzene and not naphthalene. The same may be said of the absorption of diphenyl picrate. These facts indicate that the considerable displacement of the absorption band in the case of naphthalene and its homologs is caused by the character of the conjugated condensed structure. The peculiarities of the condensed structures of tricyclic aromatic compounds are indicated by the essential difference in the absorption of phenanthrene and anthracene picrates. Figure 2 shows the absorption curves we obtained for these substances in the visible and part of the ultraviolet regions of the spectrum. The greater complexity of the absorption curve of anthracene picrate in the ultraviolet region is explained by the superposition of the absorption of anthracene itself [7] on the absorption maximum of picric acid.

Thus, as a result of the work it was found that the formation of picrates of aromatic hydrocarbons causes a displacement in the longwave edge of the absorption band of picric acid, whose value depends on the nature of the hydrocarbon and the concentration of the solution. With an increase in the number of alkyl groups in the hydrocarbon molecule, the displacement of the absorption band edge increases regularly, while an increase in the complexity of the alkyl groups, like a change in their position in the cyclic system, does not essentially affect the value of the displacement of the absorption band.

The displacement of the absorption band edge at a definite optical density or the value of the absorption at a definite wavelength may be used for determining the aromatic hydrocarbons spectrophotometrically or colorimetrically.

The authors would like to thank L. A. Mukhamedova and E. A. Robinson for providing alkylnaphthalenes and certain other compounds that they had prepared.

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INVESTIGATIONS IN THE FIELD OF BORON COMPOUNDS

REACTIVITY OF TRIALLYLBORON

Academician A. V. Topchiev, Ya. M. Paushkin,
A. A. Prokhorova, and M. V. Kurashev

Up to the present time there have been few investigations of boron compounds with a hydrocarbon radical with a double bond. There is information in the literature [1] on the reaction of β-chlorovinyl derivatives of boron with water, alcohol, and piperidine. The addition of bromine to tributenylboron is also known [2] and here the bromine was not added completely (calculated % Br, 73.14; found % 46.37; 45.47). There is no other information in the literature. We were interested in studying the reactivity of triallylboron, whose preparation we described in a previous communication [3]. Triallylboron was treated with a carboxylic acid, an alcohol, and an aldehyde. In all the reactions studied, triallylboron reacted very vigorously at room temperature with the compounds listed with considerable evolution of heat from the reaction mixture. The interaction of triallylboron with glacial acetic acid formed diallylboron acetate and propylene according to the equation:

$$(C_3H_5)_3B + CH_3COOH \rightarrow (C_3H_5)_2BOCOCH_3 + C_3H_6.$$

Triallylboron formed the diethyl and diallyl esters of allylboric acid with ethyl and allyl alcohols, respectively:

$$(C_3H_5)_3B + 2C_2H_5OH \rightarrow C_3H_5B(OC_2H_5)_2 + 2C_3H_6.$$
$$(C_3H_5)_3B + 2C_3H_5OH \rightarrow C_3H_5B(OC_3H_5)_2 + 2C_3H_6.$$

The interaction of triallylboron with acetaldehyde yielded the ethyl ester of diallylboric acid according to the equation:

$$2(C_3H_5)_3B + 2CH_3CHO \rightarrow 2(C_3H_5)_2BOC_2H_5 + C_3H_6.$$

Triallylboron reacted readily with bromine. However, the addition of bromine at room temperature took time. Thus, bromine was very rapidly added to two allyl radicals, while the addition of bromine to the third radical proceeded slowly. The reaction proceeded according to the equation:

$$(C_3H_5)_3B + 3Br_2 \rightarrow (C_3H_5Br_2)_3B.$$

After 1-1.5 hours, about 70% (of the theoretical amount) of bromine had been added, 95% after 10 days and the theoretical amount only after a month.

The molecular structure of tricovalent boron compounds have a characteristic trait, namely, the deficiency of an electron pair at the boron. Trialkyl derivatives of boron combine with donors which are capable of making

up the electron pair deficiency in the boron octet with their own free electron pair. A large number of complex compounds is known for saturated trialkylborons (triarylborons). However, up to now there has been little information in the literature on complexes of unsaturated boron compounds with amines. We prepared the complex of triallylboron with pyridine.

The reaction proceeded with considerable heat evolution and the formation of a complex:

$$B(C_3H_5)_3 + C_5H_5N \rightarrow B(C_3H_5)_3 \cdot C_5H_5N.$$

The properties of the organoboron compounds synthesized are given in Table 1.

TABLE 1

Some Physicochemical Properties of the Organoboron Compounds Synthesized

Compound	B. p., °C/mm	Yield, %	Elementary composition, %							
			calculated				found			
			C	H	B	Br	C	H	B	Br
$C_3H_5BOCOCH_3$	138–140°	46.9	63.15	7.24	8.55	—	62.78	8.01	8.17	—
$C_3H_5B(OC_3H_5)_2$	43–46°/10	52.0	59.15	10.56	7.76	—	59.31	10.83	7.38	—
							59.27	10.77	7.56	—
$C_3H_5B(OC_3H_5)_2$	50–51°/8	58.0	65.06	9.04	6.62	—	64.89	9.16	6.63	—
$(C_3H_5)_2BOC_2H_5$	43–45°/7	56.4	69.66	10.83	7.97	—	69.90	11.05	7.92	—
							69.91	11.10	7.91	—
$(C_3H_5Br_2)_3B$	—	—	17.59	2.44	1.79	78.18	17.14	2.50	1.74	78.82
							17.10	2.61	1.78	78.98
$B(C_3H_5)_3C_5H_5N$	115–118°/4	—	78.87	9.39	5.18	—	78.61	9.03	5.18	—
							78.55	9.92	5.18	—

EXPERIMENTAL

All experiments were carried out in nitrogen, carefully freed from oxygen and oxygen-containing substances.

1. Preparation of triallylboron. Triallylboron was prepared by the procedure we described previously [3]. In the reaction we used 48 g of magnesium, 80 g of allyl bromide, 37 g of boron trifluoride etherate, and 500 ml of absolute ether. With this ratio of reagents it was possible to obtain triallylboron in up to 92% yield. The triallylboron synthesized was a clear, colorless liquid, boiling over the range 62-65°/15 mm and having d_4^{20} 0.7178, and a mol. weight of 134, 136 (calculated 134).

$B(C_3H_5)_3$. Found %: C 80.16; H 11.39; B 8.45
Calculated %: C 80.6; H 11.19; B 8.21

2. Interaction of triallylboron with acetic acid. Glacial CH_3COOH (3.55 g) was added dropwise to 7.88 g of triallylboron. The gas thus liberated was trapped with a CCl_4 solution of bromine, which was rapidly decolorized. The solution thus obtained was washed with sodium carbonate solution and water until neutral and dried over fused $CaCl_2$. Removal of the CCl_4 yielded 1,2-dibromopropane with b. p. 140.5°, n_D^{20} 1.5322 (literature data: b. p. 141.6°; n_D^{20} 1.5367). After removal of the CH_3COOH, the diallylboron acetate (46.9% yield) boiled at 138-140° and appeared as a clear, colorless liquid.

$(C_3H_5)_2BOCOCH_3$. Found %: C 62.78; H 8.01; B 8.17
Calculated %: C 63.15; H 7.24; B 8.55

3. Interaction of triallylboron with ethyl alcohol. To 3.81 g of triallylboron was added 2.61 g of absolute ethyl alcohol. The reaction mixture evolved heat strongly. After removing the excess alcohol in vacuum, we distilled a clear, colorless liquid with b. p. 43-46°/10 mm, which was the diethyl ester of allylboric acid (52% yield). The propylene liberated was trapped with a CCl_4 solution of bromine.

	Found %:	C 59,31;	59,27;	H 10,83;	10,77;	B 7,38;	7,58
$C_3H_5B(OC_3H_5)_2$.	Calculated %:	C 59,15;		H 10,58;		B 7,74	

4. Interaction of triallylboron with allyl alcohol. Allyl alcohol (4.7 g) was added dropwise to 5.5 g of triallylboron. The diallyl ester of allylboric acid distilled at 50-51°/6 mm as a clear, colorless liquid (58% yield). The propylene liberated during the reaction was trapped with a CCl_4 solution of bromine.

	Found %:	C 64,83;	H 9,28;	B 6,63
$C_3H_5B(OC_3H_5)_2$.	Calculated %:	C 65,08;	H 9,04;	B 6,62

5. Interaction of triallylboron with acetaldehyde. The interaction of 8.8 g of triallylboron with 3 g of acetaldehyde formed the ethyl ester of diallylboric acid (58.4% yield), which boiled at 48-49°/7 mm and appeared as a clear liquid.

	Found %:	C 69,01;	69,00;	H 11,05;	11,10;	B 7,02;	7,18
$(C_3H_5)_2BOC_2H_5$.	Calculated %:	C 69,58;		H 10,83;		B 7,97	

6. Interaction of triallylboron with bromine. To 0.8 g of triallylboron was added 2.1 g of bromine in 10 ml of CCl_4. A slight excess of bromine was added. The sample in the CCl_4 solution of bromine was left for 1 month. The theoretical amount of bromine was added during this time. The CCl_4 was removed in vacuum. Tris-(1,2-dibromopropyl)-boron was a dark brown, immobile liquid with a sharp smell.

	Found %:	C 17,14;	17,10;	H 2,30;	2,61;	B 1,24;	1,23;	Br 78,83;	78,98
$(C_3H_5Br_2)_3B$.	Calculated %:	C 17,59;		H 2,44;		B 1,79;		Br 78,18	

7. Complex of triallylboron with pyridine. Pyridine (1.25 g) was added dropwise to 2.1 g of triallylboron (molar ratio of 1:1); there was quite considerable heat evolution. The excess pyridine was removed in vacuum and the reaction product vacuum distilled. A clear, colorless, oily liquid with b. p. 116-118/4 mm distilled. Elementary analysis confirmed the formation of a complex:

	Found %:	C 78,61;	78,55;	H 9,93;	9,92;	B 5,16;	5,18
$B(C_3H_5)_2C_5H_5N$.	Calculated %:	C 78,87;		H 9,39;		B 5, 16	

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INTERMEDIATE STAGES IN THE SYNTHESIS OF TETRACYCLINES

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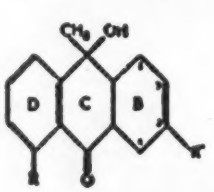
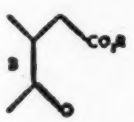
In 1956 we synthesized [1] tricyclic ketols of type (I), which are analogous to the tetracyclines (III) with respect to the structure of two rings and have a reactive double bond in the 2,3-position in the third ring; similar compounds were also obtained by Inhoffen, Muxfeldt et al., [2] in 1957. In developing these investigations, we studied the addition of different reagents to the 2,3 double bond of compounds (I) so as to introduce into their molecules the active functional groups required to produce in ring B the γ-keto ester grouping (II) and then to build up ring A of tetracyclines by the method we developed previously [3].



I



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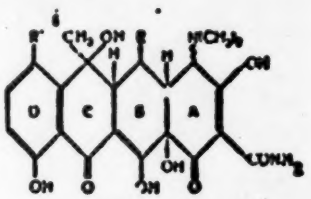


III

As the investigations showed, compounds (I) reacted readily with typical electrophilic reagents such as Hal_2, RCO_3H and HOHal to give a high yield of the corresponding dihalo derivatives, epoxides, halohydrins and halo ketones (the constants and analysis data of the compounds synthesized are presented in Table 1).

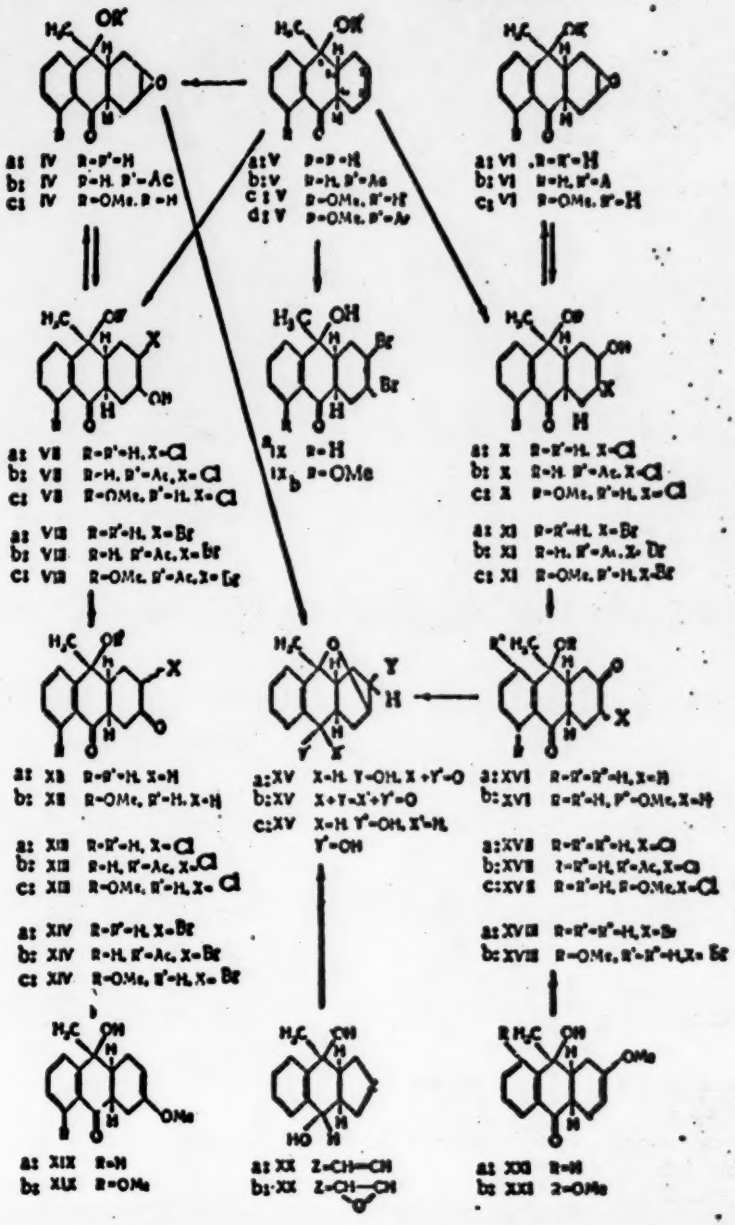
Thus, bromination of compounds of type (V) with bromine in $CHCl_3$ at -60° gave a 60-70% yield of the corresponding dibromides (IX) and oxidation of the same compounds (V)* with $PhCO_3H$ in $CHCl_3$ (20°, 16 hours) gave an 85-95% yield of α-epoxides of type (IV). Both reactions proceeded stereospecifically and led to compounds containing the electrophilic substituent in position 3a.

A similar steric direction was also observed in the addition to substances of type (V) of HOCl or HOBr by the action of tert.-BuOCl in aqueous acetone at 20° or $(CH_2CO)_2NBr$ on a 0.01 N aqueous acetone solution of H_2SO_4 at 0°. The first of these reactions led to the formation of chlorohydrins of type (X) (75-85% yield) and the second (with the same yield), to a mixture of isomeric bromohydrins of the type (VIII) and (XI) in a ratio of approximately 1:2; thus, in all cases addition occurred at positions 2β and 3α.

Bromohydrins of type (VIII) and also chlorohydrins of type (VII) may also be prepared in satisfactory yield by another method, namely ring-opening of α-epoxides (IV) by means of Py.HBr or Py.HCl in alcohol solution (boiling for 10-15 minutes). The reverse reaction of closure of the oxide ring by the action of 0.1 N KOH in

*The previously undescribed acetoxyketones (Vb) and (Vd) were obtained from the HalMg-alcoholates of the ketols (Va) and (Vc) by acetylation with Ac_2O in benzene at 20°.

70% dioxane on the halohydrins (VII) and (VIII) (20°, 30 minutes) led to a high yield of the original α-epoxides (IV).



Under these conditions the isomeric halohydrins of type (X) and (XI) gave almost quantitative yields of the stereoisomeric β-epoxides of type (VI), which in their turn could be opened with pyridine hydrohalides to give the original chloro- and bromohydrins (X) and (XI).

The addition of HOCl to ketols (XIX) and (XXI), which are enol ethers, or the chlorination of these compounds with chlorine in $CHCl_3$ at -50° with subsequent hydrolysis by water in the presence of $CaCO_3$ at 20° led to unstable chloro ketones of types (XIII) and (XVII) in about 80% yield. The latter and also the equally stable bromo ketones of types (XIV) and (XVIII) could also be obtained in 75-90% yield by oxidation of the corresponding chloro- and bromohydrins of types (VII), (VIII), (X) and (XI) with chromic acid in 80% AcOH (30°, 30 minutes).

TABLE 1

Compound	M. p. or decomp. p. and recrystallization solvent	λ_{max}^{EtOH}, mμ (log ε)	Found %			Calc. %		
			C	H	Hal	C	H	Hal
IV a	138°(EtOH)	249, 289 (4.03, 3.22)	73.49	6.74		73.75	6.84	
IV b	146°(C_6H_6-CH_3)	247, 285 (4.04, 3.16)	71.31	6.48		71.31	6.34	
IV c	211°(50% EtOH)	255, 317 (4.12, 3.56)	70.34	6.76		70.05	6.61	
V a	174°(EtOH)	242, 287 (3.85, 3.16)	73.7	6.55		73.83	6.71	
V d	209°(EtOH)	258, 303 (4.03, 3.69)	71.81	6.58		71.93	6.71	
VI a	141°(50% EtOH)	250, 290 (4.03, 3.17)	74.01	6.70		73.75	6.60	
VI b	101°(50% EtOH)	248, 288 (4.18, 3.16)	71.25	6.58		71.31	6.34	
VI c.	174°(AcOEt)	228, 297, 317 (3.97, 3.43, 3.38)	69.04	6.60		70.05	6.61	
VII a	153°(C_6H_6)	252, 291 (4.01, 3.19)	64.99	6.22	12.62	64.17	6.10	12.64
VII b	161°(C_6H_6)	251, 288 (4.02, 3.12)	63.65	6.18	10.65	63.25	6.03	10.98
VII c	178°(AcOEt)	257, 317 (3.92, 3.55)	61.49	5.58	11.03	61.63	6.10	11.41
VII a	164°(EtOH)	252, 292 (4.12, 3.21)	64.99	6.20	24.37	65.01	6.27	24.57
VIII b	152°(75% EtOH)	251, 288 (4.11, 3.21)	65.55	6.32	21.61	65.85	6.22	21.78
VIII c*	179°(50% EtOH)	253, 290, 318 (3.85, 3.44, 3.65)	61.66	5.67	21.37	61.45	5.67	21.43
IX a	140°(AcOEt)	249, 290 (4.05, 2.82)	46.72	6.47	41.09	46.47	6.15	41.18
IX b	174°(EtOH)	250, 319 (3.92, 3.66)	46.19	6.36	29.26	45.96	6.34	29.22
X a	211°(C_6H_6)	250, 291 (3.93, 3.21)	64.04	6.24	12.65	64.17	6.10	12.64
X b	155°(70% EtOH)	250, 288 (4.04, 3.15)	63.14	6.01	11.09	63.25	5.83	10.98
X c	210°(EtOH)	253, 316 (4.08, 3.63)	62.11	5.82	11.63	61.83	5.10	11.41
XI a	179°(EtOH)	250, 290 (4.12, 3.32)	65.05	6.34	21.91	65.40	6.27	24.57
XI b	157°(65% EtOH)	249, 288 (4.05, 3.17)	65.37	6.51	21.64	65.55	6.22	21.78
XI c	205°(EtOH)	228, 298, 317 (3.47, 3.53, 3.41)	59.91	5.55	22.10	54.02	5.30	22.10
XII a	121°(C_6H_6)	250, 291 (4.03, 3.17)	73.58	6.65		73.75	6.63	
XII b	192°(50% EtOH)	256, 319 (3.91, 3.67)	70.19	6.36		70.05	6.61	
XIII a	65°($CHCl_3$—hexane)	249, 290 (4.01, 3.17)	65.06	5.99	12.69	64.63	5.43	12.78
XIII b	106°(dioxane-hexane)	244, 297 (4.25, 3.25)	63.56	5.69	11.10	63.65	5.34	11.05
XIII c	65°(AcOEt)	257, 317 (4.22, 3.05)	62.15	5.67	11.72	62.24	5.55	11.48
XIV a	64°($CHCl_3$ — hexane)	251, 291 (4.03, 3.19)	55.84	4.81	24.63	55.73	4.70	24.72
XIV b	57°($CHCl_3$ — hexane)	251, 296 (3.92, 3.22)	55.64	4.85	22.04	55.27	4.69	21.88
XIV c	70°(dioxane-hexane)	255, 317 (3.85, 3.63)	54.13	4.85	22.49	54.41	4.83	22.63
XV a	135°(C_6H_6)	247, 283 (3.44, 2.05)	74.15	6.72		73.75	6.60	
XV b	152°(EtOH)	249, 288 (4.00, 3.09)	74.59	6.07		74.38	5.83	
XV c	150°(EtOH)	280 (2.26)	73.03	7.12		73.14	7.37	
XVI a	125°(C_6H_6)	249, 291 (3.63, 3.07)	74.11	6.40		73.75	6.60	
XVI b	161°(50% EtOH)	222, 255, 313 (4.21, 3.81, 3.51)	69.95	6.71		70.05	6.61	
XVII a	85°(C_6H_6)	252, 292 (4.04, 3.22)	64.80	5.78	13.01	64.63	5.43	12.78
XVII b	119°(C_6H_6)	250, 288 (4.07, 3.15)	63.25	5.63	11.00	63.65	5.34	11.05
XVII c	121°(C_6H_6)	253, 296, 313 (4.20, 3.88, 3.25)	62.66	5.78	11.30	62.24	5.55	11.48
XVIII a	65°($CHCl_3$—heptane)	250, 290 (4.02, 3.10)	55.31	4.57	25.22	55.73	4.70	24.72
XVIII b	69°($CHCl_3$—hexane)	253, 318 (3.93, 3.68)	54.46	5.23		54.61	4.85	
XX a	244°(EtOH)	262 (2.32)	77.56	7.77		78.23	7.83	
XX b	162°(EtOH)	261 (2.29)	74.10	7.44		73.14	7.37	
XXII	127°(C_6H_6)	223, 260 (3.72, 4.19)	68.53	6.90		68.38	6.78	
XXIII*	164°(H_2O)	247, 287 (4.07, 3.15)	59.56	6.35		59.04	6.05	
XXIV	160°(50% EtOH)	249, 289 (4.05, 3.11)	74.09	6.40		74.38	5.83	
XXV	272°(EtOH)		61.19	5.05		60.70	5.39	

*Monohydrate.

Halo ketones of types (XIII), (VIV), (XVII) and (XVIII) were readily dehalogenated with Zn dust in AcOH at 30° to form the corresponding hydroxy diketones of types (XII) and (XVI); the same hydroxy diketones were obtained in 80-90% yield by hydrolysis of ketols (XIX) and (XXI) with a 0.03 N solution of HCl in 70% alcohol at 40°.

This conversion of halohydrins (VII), (VIII), (X) and (XI) through the halo ketones (XIII), (XIV), (XVIII) and then through the hydroxy diketones (XII) and (XVI) to the enol ethers (XIX) and (XXI) are a demonstration of the structures of all the compounds listed. As regards the steric structure of these substances, this was established in the following way. The action of tert.-BuOK on epoxide (IVa) produced intramolecular opening of the α-oxide ring and the latter was converted into the hydroxy keto oxide (XVa), which was then oxidized to diketo oxide (XVb), which in its turn was obtained by synthesis from chloro ketone (XVIIa) by treating the latter with bases. A similar conversion into the 3,9-oxide (XVc) was also achieved with the dihydroxyepoxide (XXb), which was obtained from ketol (Va) by reduction with $LiAlH_4$ to glycol (XXa) and subsequent oxidation with $PhCO_3H$. As an examination of molecular models shows, the formation of such a 3,9-oxide bridge is only possible with cis-coupling of rings B and C and the OH group at C_9 in a trans position with respect to the hydrogen atoms at $C_{10\alpha}$ and $C_{8\alpha}$. Since the conversion (VA) → (XXa) → (XXb) → (XVc) → (XVb) proceeds under conditions which

exclude inversion of the asymmetric centers 4a, 9 and 9a, evidently all the substances described in the present work, like the 3,9-oxides (XV), must have a 4aαH, 9β OH and 9aαH structure and in this case a cis-coupling of the hydroaromatic rings B and C is apprently most stable (see [1]). The configuration of the rest of the asymmetric centers, i. e., 2 and 3, follows from the tendency of the halohydrins (VII), (VIII), (X) and (XI) to convert readily into the corresponding epoxides (a trans-diaxial disposition of the OH and Hal) and the incapacity of the β-epoxides (VI) to isomerize into 3,9-oxides (the impossibility of trans-closure of an epoxide ring under attack from the β-region).

The tricyclic compounds of types (VII) – (XIV) and (XVI) – (XVIII) we synthesized contained in positions 2 and (or) 3 one or two active functional groups by means of which it is possible to introduce into ring B substituents (a malonyl residue, for example), which may then be converted into the "upper" part of ring A of tetracyclines. Thus, dibromide (IXa) condensed with malonic ester in the presence of 2 equivalents of EtONa with the formation of the unsaturated malonate (XXII) and β-epoxide (VIa) was converted into hydroxydicarboxylic acid (XXIII) by reaction with sodiomalonic ester and subsequent hydrolysis. Similarly, condensation of sodiomalonic ester with chloro ketone (XIIIa) formed, in addition to 2,9-oxido ketone (XXIV), the corresponding ketomalonate, which was isolated as the bis-p-nitrophenylhydrazone (XXV).

Thus, the tricyclic ketols with active functional groups in ring B we synthesized open up the possibility of building up ring A of tetracyclines.

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SOME REACTIONS IN THE CHAINS OF VINYL ALCOHOL COPOLYMERS

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The physical properties of copolymers depend both on the forces acting between the macromolecules and on those inside the molecules between their different elements. The interaction within the macromolecule chain determines its flexibility and the interaction between the macromolecules, the mechanical strength of the polymer. As is known, the intermolecular reactions are determined by a) dipole forces, b) induction forces, c) dispersion forces and d) hydrogen bonds.

The cross-linking of linear macropolymer chains with primary valence bonds (bearing in mind that the number of such cross-links is limited and does not convert the polymer into a globular one) has the same qualitative effect as an increase in the interparticle reaction forces (achieved, for example, by introducing polar groups into the polymer structure). Both the introduction of dipoles and the formation of bridges between the chains raise the vitrification point, moduli of rigidity and high elasticity, tensile strength and hardness of the polymer and decrease its elongation on breaking and impact resistance. As regards the mechanism of polymer rupture, at a sufficient degree of polymerization the rupture may occur by an intramolecular mechanism, regardless of the presence of bridges between the chains.

There is, however, one very important basic difference in the properties of a polymer which are determined by the interparticle reaction forces (such as dipole forces and hydrogen bonds) on the one hand, and by valence bridge bonds, on the other. The former are strongly dependent on temperature and an increase in the latter sharply weakens them. The valence bridge bonds hardly depend on temperature over a wide range.

To modify the properties of high polymers by changing their chemical structure, it is practically necessary either to introduce polar groups into the chain or to establish bridge bonds. The direction of the changes in the properties would be the same in both cases but, for example, the thermal stability of a polymer cross-linked by chemical valence bonds would be maintained over a considerably greater range of temperatures than that of a polymer containing strong dipoles.

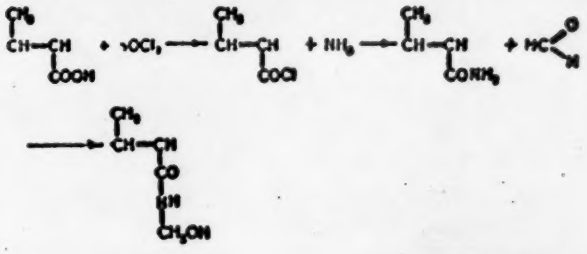
The procedure of forming cross-linked, three-dimensional polymers by establishing bridge valence bonds between chains is preferable to using intermolecular forces in a number of cases.

Cross-linked polymers may be formed in various ways, of which the most important are the following: a) copolymerization of di- and polyreactive monomers (by a radical mechanism); b) interaction of functional groups in the structure of the polymer and c) the use of different radiations (mainly γ-rays).

The processes of preparing cross-linked polymers by copolymerization of vinyl and divinyl (diallyl etc.) monomers have been widely developed. The disadvantage of this method is that the three-dimensional copolymer formed reaches its gelatinization point when there is still a large percent of a sol fraction, which naturally lowers the thermal and mechanical indices of the polymeric material. Such a process proceeds further towards completion when the second (divinyl) component of the reaction is incapable of homopolymerization. In this case the space lattice of the copolymer is formed only through heteropolymerization. The author has proposed and, together with his co-workers, has applied a series of new divinyl cross-linking agents, which give good results in heteropolymerization with acryl derivatives and vinyl esters. The diallyl acetals of various aldehydes (formal, ethylal and butyral) were proposed as effective cross-linking agents by the author together with L. A. Arbuzova and S. A. Plotkina [1] and studied thoroughly in copolymerization with vinyl acetate (together with L. Santo [2]).

Another group of particularly effective cross-linking agents for vinyl esters was first synthesized and applied by the author together with E. M. Lavrent'eva and K. S. Podgorskaya [3]. Dicrotonamidodimethyl ether and bis-crotonamidomethylene are such cross-linking agents. These derivatives of crotonic acid are incapable of homopolymerization but form heteropolymers readily with vinyl acetate and other vinyl esters and even the addition of 0.2-0.1 mol. %.of the cross-linking agent gives transparent, infusible, solid copolymers, without the property of cold yield inherent in poly-(vinyl acetate). However, the use of these new processes of copolymerization with diallyl acetals and tetra-reactive crotonyl derivatives to obtain cross-linked three-dimensional polymers still does not eliminate the disadvantages inherent in the process of three-dimensional copolymerization and in the mechanism of establishing bridge bonds.

A better process for the formation of polymers is the cross-linking of long linear macromolecules by condensati' of reactive functional groups included in the chain. Usually in this case, not only are bridge bonds formed between ch-ins but also rings in the chain. In order to eliminate this phenomenon, which is undesirable for a number of purposes for which the polymers are designated, the functional groups may be introduced into the chain by heteropolymerization. This makes it possible to obtain a copolymer chain which does not contain adjacent units with functional groups. With E. M. Lavrent'eva and K. S. Podgorskaya, the author proposed and carried out an interesting example of such processes, namely, the copolymerization of vinyl acetate and other vinyl esters with hydroxymethylcrotonamide and crotonamide. The authors synthesized hydroxymethylcrotonamide for the first time by reacting crotonyl chloride with paraformaldehyde in a carbon tetrachloride medium [4] according to the scheme.



$C_5H_9O_2N$; mol. weight 115 (cryoscopically), N – 12.18 (theoretical 12.17%) d_{15}^{20} 1.1662; n^{20} 1.5164, m. p. 88°; yield 80-85% of theoretical (recrystallized from benzene). Copolymerization with hydroxymethylcrotonamide may be carried out in block or in a solvent in the presence of such radical polymerization initiators as benzoyl peroxide, acetyl benzoyl peroxide and azoisobutyrodinitrile. We mostly use copolymerization in methanol with distillation of the unreacted vinyl acetate and the reaction mixture maintained at a constant volume by the gradual addition of methanol.

The linear heteropolymers thus obtained are thermosetting and form infusible and insoluble polymers with a three-dimensional structure when heated.

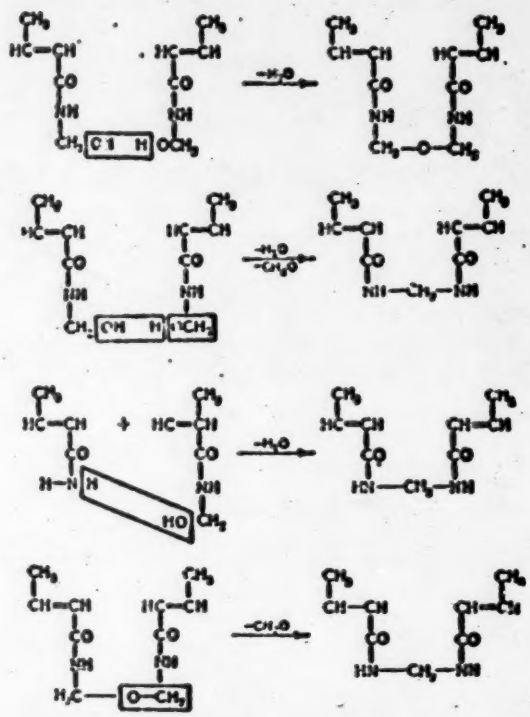
The author and B. L. Trukhmanova studied the mechanism of radical copolymerization of vinyl acetate with crotonamide and hydroxymethylcrotonamide and established the copolymerization constants of these systems (determined by the selected curves method).

For the crotonamide – vinyl acetate system $r_1 = 0.01 \pm 0.01$ and $r_2 = 2.0 \pm 0.5$ and for the hydroxymethylcrotonamide – vinyl acetate system $r_1 = 0.01 \pm 0.01$ and $r_2 = 0.45 \pm 0.1$.

From the data obtained it was established that the relative activities of crotonic acid and hydroxymethylcrotonamide towards the vinyl acetate radical were of the same order, but this was less in the case of the crotonamide monomer, which may be explained by the difference in chemical structure of the monomers and the effect of the penultimate unit. The relative activities of the vinyl acetate monomer towards the radicals of crotonic acid and its amide and hydroxymethylamide are the same. Thus, this practically excludes the possibility of hydroxymethylcrotonamide units occurring next to each other in the copolymer chain. When heteropolymers of vinyl acetate with hydroxymethylcortonamide are heated, the N-hydroxymethyl groups of adjacent chains react with each other to form an ether or a methylene bond between the chains.

The reaction mechanism was first studied on monomers. Heating hydroxymethylcrotonamide in aromatic hydrocarbons without catalyst and with the water formed in the reaction removed by distillation with solvent vapor gave dicrotonamidodimethyl ether. Heat treatment of dicrotonamidodimethyl ether produced elimination of formaldehyde and gave bis-crotonamidomethylene. The latter may also be formed by heating an equimolecular mixture of hydroxymethylcrotonamide and crotonamide in xylene without catalysts. The reactions gave yields close to theroretical.

The reaction schemes and the properties of the compounds obtained are as follows: Mol. weight (by Rast's method) 212; N – 13.19% (theoretical 13.20%); bromine number 151.9 (theoretical 151.0); n_D^{20} 1.5557; d_{20}^{20} 1.1312; m. p. 136°; yield 97% of theoretical.



Mol. weight (by Rast's method) 182; N – 15.33% (theoretical 15.38%); bromine number 175.6 (theoretical 175.8); n_D^{20} 1.5262; d_{20}^{20} 1.0854; m. p. 152°; yield 95-99% of theoretical.

It was proved experimentally (by the reaction of the copolymer in toluene solution without catalyst) that these reactions occur in copolymers practically completely with the evolution of the theoretical amount of water. Catalytic methanolysis of the copolymer of vinyl acetate and hydroxymethylcrotonamide converts it into a copolymer of vinyl alcohol and hydroxymethylcrotonamide which is soluble in water and has the degree of thermal reactivity as the copolymer with vinyl acetate. The copolymers of vinyl acetate or vinyl alcohol with hydroxymethylcrotonamide are converted into an infusible and insoluble state quite rapidly [5]. Thus, a film of vinyl alcohol copolymer containing 3 mol.% of hydroxymethylcrotonamide became insoluble in cold and hot water when heated at 130° for 20 minutes and at 180° for 5 minutes, while a film of pure polyvinyl alcohol remained soluble after the same treatment. The same effect was achieved on using mixtures of copolymers with crotonamide and with hydroxymethylcrotonamide.

The changes in the mechanical properties of films on the introduction of hydroxymethylcrotonamide units into the copolymer chain and on heat treatment in comparison with the properties of polyvinyl alcohol films are characterized by the data in Table 1.

New copolymers of vinyl esters and vinyl alcohol with hydroxymethylcrotonamide (and crotonamide) may find wide practical application. Heat-treated copolymers have a considerably higher mechanical strength than pure polyvinyl alcohol and are completely insoluble in both cold and boiling water.

TABLE 1

	Tensile strength, kg/cm²	Relative elongation, %	Solubility in cold water	Solubility in hot water
Polyvinyl alcohol	750	2.5	Incompletely	Completely
Copolymer with 3 mol. % of hydroxymethylcrotonamide.....	1050	10	Completely	Completely
The same, heated copolymer....	1125	10	Insoluble	Insoluble even on boiling

Vinyl acetate copolymers with 1-3 mol. % of hydroxymethylcrotonamide, which are soluble in the usual organic solvents, may be used as lacquers. After heat treatment, the coatings obtained are outstanding in hardness, heat resistance, insolubility and high surface luster. Similar water-soluble vinyl alcohol copolymers also form quite water-stable films after heat treatment when used as coatings. The properties of such films makes it advantageous to use them in certain special fields.

By the use of copolymers of vinyl alcohol with hydroxymethylcrotonamide, articles may be prepared that are quite stable to the action of ligroin and quite water resistant without further processing.

Thermosetting vinyl alcohol copolymers (such as copolymers with hydroxymethylcrotonamide and ternary copolymers of vinyl alcohol with hydroxymethylcrotonamide and crotonamide or mixtures of copolymers of vinyl alcohol with hydroxymethylcrotonamide and vinyl alcohol with crotonamide) are quite valuable for preparing synthetic thermosetting fibers of a particular type [6]. After heat treatment, such a fiber becomes insoluble in water, does not require formaldehyde processing and is usually stronger than "Vinylon".

Thus, when a linear copolymer is made thermosetting by the addition of units containing reactive functional groups that do not occupy adjacent positions in a chain, it has great possibilities for technical use.

In this connection the new group of heteropolymers with crotonic acid derivatives are especially valuable for the production of coatings, plastic and synthetic fibers.

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CONVERSION OF FURANIDINE AND TETRAHYDROPYRAN INTO THE CORRESPONDING SILICON-CONTAINING HETEROCYCLES; CONVERSION OF THE LATTER INTO SULFUR-CONTAINING HETEROCYCLES

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(Presented by Academician A. N. Nesmeyanov, April 27, 1959)

At the end of 1957, Gilman and Wittenberg [1] reported that by prolonged heating (3-6 days at 250-260°) of diphenylsilane with sulfur-containing heterocycles of an aromatic nature such as phenoxathiin, phenothiazine and thianthrene (until the evolution of hydrogen sulfide ceased), they obtained very low yields of 10,10-diphenyl-phenoxasilin (2%), -phenazasilin (1.2%) and -phenothiasilin (4.7%), respectively. Thus, this reductive reaction, which proceeded with great difficulty, did not involve either the oxygen atom or the imino group, cyclically attached to two benzene rings in the condensed system of phenoxathiin and phenoxathiazine, respectively.

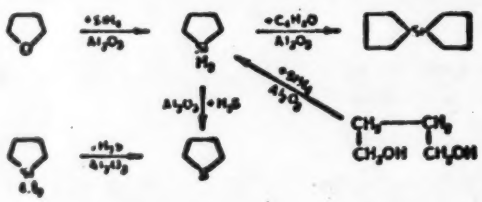
Using the catalytic method for the interconversion of heterocycles, discovered by one of us [2], we passed furanidine over aluminum oxide in a stream of monosilane at 375° and obtained tetramethylenesilane (4%) together with ditetramethylenesilane (1.5%), the conversion product of furanidine under the action of the tetramethylenesilane formed.

In connection with this, we passed a mixture of furanidine and tetramethylenesilane over aluminum oxide and obtained ditetramethylenesilane (4.5%).

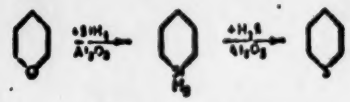
It was impossible to achieve a similar conversion of furanidine under the action of ethylsilane as the latter decomposed noticeably at 325° and completely at 350° in contact with aluminum oxide.

We also obtained tetramethylenesilane by combined catalytic dehydration of butanediol-1,4 and monosilane under the same conditions.

Under the action of hydrogen sulfide on tetramethylenesilane and tetramethylene-chlorosilane, the ring silicon atom was replaced by sulfur and we obtained thiophane (14% and 4%, respectively); the reverse change under the action of monosilane did not occur at all, though the evolution of hydrogen sulfide was observed.



When treated with monosilane in contact with aluminum oxide at 375°, tetrahydropyran was converted into pentamethylenesilane (9.5%); when the latter was treated with hydrogen sulfide under the same conditions, it was converted into tetrahydrothiopyran (24%).



EXPERIMENTAL

Tetramethylenesilane*. a) 20 g of butanediol-1,4 was passed over aluminum oxide at 375° in a stream of monosilane. We obtained 0.6 g (2.6%) of tetramethylenesilane (0.5 g was obtained at 350°; complete decomposition occurred at 400°): b. p. 70-71° (749 mm), n_D^{20} 1.4467, d_4^{20} 0.8039, MR_D 28.60, $C_4H_{12}Si$. Calculated: 28.67. Literature data [4]: b. p. 70.7-70.8° (733.5 mm), n_D^{20} 0.8065; [5] b. p. 70-71° (760 mm); n_D^{25} 1.4440 d_4^{25} 0.8000.

b) 20 g of furanidine was passed over aluminum oxide at 375° at a rate of 0.4-0.5 ml/min. in a stream of monosilane. Distillation of the dried catalyzate yielded 0.9 g (4%) of tetramethylenesilane (average yield from nine experiments with the catalyst regenerated with air after each experiment): b. p. 70-71° (750 mm), n_D^{20} 1.4482, d_4^{20} 0.8049, MR_D 28.63, $C_4H_{12}Si$. Calculated: 28.67.

$C_4H_{12}Si$.	Found %:	C 55,57;	55,61;	H 11,53.	11,53;	Si 32,39; 32,45
	Calculated %:	C 55,73;		H 11,69;		Si 32,58.

0.5 g (1.5%) of ditetramethylenesilane (average yield from nine experiments) was also obtained: b. p. 174-175° (750 mm), n_D^{20} 1.4860, d_4^{20} 0.9048. MR_D 44.52, $C_8H_{18}Si$. Calculated: 44.54.

$C_8H_{18}Si$.	Found %:	C 60,89;	60,81;	H 14,09;	14,14;	Si 24,62; 24,57
	Calculated %:	C 60,93;		H 14,26;		Si 24,78

Literature data [4]: b. p. 172-174° (750 mm), n_D^{20} 1.4863, d_4^{20} 0.9043; [5] b. p. 178.5° (760 mm), n_D^{25} 0.8999.

Ditetramethylenesilane. A mixture of 10 g of tetramethylenesilane and 10 g of furanidine (1:1.1) was passed over regenerated aluminum oxide at a rate of 0.3 ml/min. in a stream of nitrogen at 375°. We obtained 0.8 g (4.5%) of product: b. p. 173-174° (750 mm), n_D^{20} 1.4870, d_4^{20} 0.9010, MR_D 44.80.

Pentamethylenesilane. 20 g of tetrahydropyran was passed over regenerated aluminum oxide at a rate of 0.4 ml/min. in a stream of monosilane at 375°. We obtained 2.5 g (9.5%) (2 g yield at 325° and 2.2 g at 350°, i.e., 8% and 8.5%): b. p. 101-102° (760 mm): n_D^{20} 1.4499, d_4^{20} 0.8191, MR_D 33.60, $C_5H_{12}Si$. Calculated: MR_D 33.28.

$C_5H_{12}Si$	Found %:	C 59,58;	59,64;	H 12,16;	12,23;	Si 27,84; 27,78
	Calculated %:	C 59,92;		H 12,07;		Si 28,01

Literature data: [5] b. p. 101-102°, n_D^{25} 1.4533, d_4^{25} 0.8189.

Thiophane. a) 20 g of tetramethylenesilane was passed over aluminum oxide at a rate of 0.6 ml/min. at 375° in a stream of hydrogen sulfide. The catalyzate was saturated with potassium hydroxide and extracted with ether. After removing the ether from the dried extracts, we obtained 3 g (14%) of product: b. p. 120° (759 mm), n_D^{25} 1.5046, d_4^{20} 0.9960, MR_D 26.10, C_4H_8S. Calculated: 26.39. The compound with mercuric chloride melted at 125-125.5° (from alcohol).

$C_4H_8S \cdot HgCl_2$.	Found %:	Hg 63,12;	63,18			
	Calculated %:	Hg 63,23				

*Using the method of B. N. Dolgov, S. N. Borisov, and M. G. Voronkov [3] and heating tetramethylenedichlorosilane with a stoichiometric amount of triethylsilane in the presence of catalytic amounts of $AlCl_3$, we obtained tetramethylenesilane in 85% yield; we obtained diethylsilane in 60% yield by reducting diethyldichlorosilane.

b) 12 g of tetramethylenedichlorosilane was passed over aluminum oxide at a rate of 0.3 ml/min. at 400° in a stream of hydrogen sulfide. We obtained 0.5 g (4%) of product (the conversion did not occur at 350°, the yield was 3.7% at 450°); b. p. 119.5-120.3° (753 mm); the compound with mercuric chloride melted at 125° (from alcohol).

$C_4H_8S \cdot HgCl_2$	Found %	: Hg 63.01; 63.15
	Calculated %:	Hg 63.23

Literature data: [6] b. p. 119.8-120° (750 mm), n_D^{20} 1.5052, d_4^{20} 0.9980.

Tetrahydrothiopyran. 8 g of pentamethylenesilane was passed over aluminum oxide at 375° in a stream of hydrogen sulfide. Treatment of the catalyzate as described above yielded 2 g of tetrahydrothiopyran: b. p. 138-139° (735 mm), n_D^{20} 1.5032, d_4^{20} 0.9774, MR_D 30.60, $C_5H_{12}S$. Calculated 3090. The m. p. of the compound with mercuric chloride was 136-137° (from alcohol). Literature data: [7] b. p. 139.4-140° (747 mm), n_D^{19} 1.5048, d_4 0.9791; m. p. of compound with mercuric chloride: 137-137.5°.

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SOME PHYSICOCHEMICAL CHARACTERISTICS OF EXCHANGE EXTRACTION

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(Presented by Academician I. I. Chernyaev, April 6, 1959)

Exchange extraction is based on reactions which occur between salts of aliphatic acids (soaps), dissolved mainly in an organic phase, and salts of mineral acids, dissolved in an aqueous phase [1]:

$$({}^1Me^{2+})_0 + ({}^2Me\,R_2)_0 \rightleftarrows ({}^1Me\,R_2)_0 + ({}^2Me^{2+})_A. \qquad (1)$$

where ^1Me and ^2Me denote the corresponding metals, R the acid residue of the aliphatic acid, $C_nH_{2n+1}COO^-$, the indexes O and A, the organic and aqueous phases (the metals can have a different valence to that indicated in Equation (1)). The equilibrium constants of Reaction (1):

$$K = [{}^1Me\,R_2]_0\,[{}^2Me^{2+}]_A / [{}^2Me^{2+}]_A\,[{}^2Me\,R_2]_0. \qquad (2)$$

where the corresponding activities are denoted by the square brackets.

Measurement of the electroconductivity of the phases and the experimental data obtained on the equilibria indicate that the soaps are not dissociated in an organic phase, but are dissociated in an aqueous one. The equilibrium conditions of metal soaps in a system containing two divalent metals are expressed by the equations:

$$[{}^1Me\,R_2]_0 / [{}^1Me^{2+}]_A\,[R^-]_A^2 = K_1; \qquad [{}^2Me\,R_2]_0 / [{}^2Me^{2+}]_A[R^-]_A^2 = K_2. \qquad (3)$$

In exchange extraction, the conditions of equilibrium of both soaps must be fulfilled simultaneously and simultaneous solution of the equations (3) gives:

$$[{}^1Me\,R_2]_0\,[{}^2Me^{2+}]_A / [{}^1Me^{2+}]_A\,[{}^2Me\,R_2]_0 = K_1 / K_2. \qquad (4)$$

From (2) and (4) it follows that $K = K_1/K_2$, i.e., the equilibrium constant of the exchange reaction is the ratio of the distribution coefficients of the soaps of the exchanging metals.

Thus, the direction of exchange reactions is controlled by the character of the distribution of the corresponding soaps. Metals whose soaps are less soluble in water pass mainly into the organic phase as soaps; metals with more soluble soaps are mainly in the aqueous phase as cations. This exchange is similar to exchange between solutions containing a cation and a precipitate (for example, $Cu^{2+} + NiS = CuS + Ni^{2+}$), but in our case the second phase is not a solid but a liquid organic phase.

A study of soap distribution between the aqueous and the organic phase (an aliphatic acid of the $C_7 - C_9$ fraction or a solution of an aliphatic acid in an inert solvent, for example, kerosene) showed that the metals may be arranged in the following series according to the increasing solubility of their soaps in water: Fe^{III}, Pb^{II}, Cu^{II}, Zn, Ni^{II}, Co^{II}, Mn^{II}, Na; the same sequence is maintained in exchange reactions; each of the metals, present in

the aqueous phase as a cation, displaces all those to the right of it in the series from the corresponding soap, dissolved in the organic phase.

A metal can be extracted into the organic phase by the addition of alkali to the system; in this case there is a linear dependence between the logarithm of the distribution coefficient of the metal α ($\alpha = y/x$, where y and x are the equilibrium concentrations of the metal in the organic and aqueous phases, respectively) and the pH of the equilibrium aqueous phase. Extraction under the action of alkali may be expressed by the following equations:

$$(Me^{2+})_A + 2(HR)_o + 2(OH^-)_A \rightleftarrows (MeR_2)_o + 2(H_2O)_A; \tag{5}$$

$$\frac{[MeR_2]_o [H_2O]^2_A}{[Me^{2+}]_A [HR]^2_o [OH^-]^2_A} = K'_s; \qquad \frac{[MeR_2]_o [H^+]^2_A}{[Me^{2+}]_A [HR]^2_o K^2_w} = K_s. \tag{6}$$

where K_W is the ionic product of water and K_s is the equilibrium constant. In the given system there occurs simultaneous distribution of the metal soaps and the aliphatic acids:

$$(Me^{2+})_A + 2(R^-)_A \rightleftarrows (MeR_2)_o; \quad (H^+)_A + (R^-)_A \rightleftarrows (HR)_A \rightleftarrows (HR)_o. \tag{7}$$

The corresponding equilibrium conditions are:

$$[MeR_2]_o / [Me^{2+}]_A [R^-]^2_A = K_d; \quad [HR]_o / [H^+]_A [R^-]_A = K_a. \tag{8}$$

By simultaneously solving the Equations (8) [or having written the reaction as $Me^{2+} + 2(HR)_o \rightleftarrows (MeR_2)_o + 2H^+$], we obtain the equilibrium conditions of the systems:

$$[MeR_2]_o [H^+]^2_A / [Me^{2+}]_A [HR]^2_o = K_{Me-H}. \tag{9}$$

Equation (9) coincides with Equation (6) so that the equilibrium constant $K_{Me-H} = K_s \cdot K^2_w$. Thus, extraction of metals with an aliphatic acid under the effect of alkali is determined by the conditions of the interdistribution of the metal of the soap and the aliphatic acid. Transposing (9), we obtain:

$$[MeR_2]_o / [Me^{2+}]_A = K_{Me-H} [HR]^2_o \cdot 1/[H^+]^2_A. \tag{10}$$

Replacing, with some approximation, the ratio of activities in the left part by the concentration ratio α and also considering that the concentration of the aliphatic acid in the organic phase is great in comparison with the concentration of the soap formed and changes very little under the experimental conditions, from (10), we obtain:

$$\log \alpha = K_s + 2\,pH. \tag{11}$$

Kolthoff and Sandell [2] and Irving et al., [3] obtained an equation of a similar type for the extraction of metals with weak organic acids, for example dithizone, by a somewhat different method.

Figure 1 shows the experimental data characterizing the extraction of Cu^{II}, Zn, Ni^{II}, Co^{II} with an aliphatic acid (the $C_7 - C_9$ fraction dissolved in kerosene with a concentration of aliphatic acid in the organic phase of 400 g/liter) under the action of NaOH. It is seen that Equation (11) is fulfilled with sufficient accuracy. As the alkali properties of the metals increase, the constants K_s decrease with the same sequence as that noted above, maintained for the metals. One may readily show that for metals with the same valence, the constant of exchange reaction (I) is determined by the constants K_{Me-H}, which characterize the extraction of each of the exchanging metals under the action of alkali. In an exchange reaction there occurs interdistribution of $^1MeR_2$ and $^2MeR_2$.

$$(^1Me^{2+})_A + 2(R^-)_A \rightleftarrows (^1MeR_2)_o, \qquad (^2Me^{2+})_A + 2(R^-)_A \rightleftarrows (^2MeR_2)_o. \tag{12}$$

and also of the aliphatic acid HR, which is in excess in the organic phase (Equation 7).

Let us examine the equilibrium conditions in the interdistribution of the soaps of each metal and the aliphatic acid; (12) and (7) together gives

$$\frac{[^1MeR_3]_o[H^+]_A^3}{[^1Me^{3+}]_A[HR]_o^3} = K_{1Me-H}; \quad \frac{[^2MeR_3]_o[H^+]_A^3}{[^2Me^{3+}]_A[HR]_o^3} = K_{2Me-H}. \tag{13}$$

The constants K_{1Me-H} and K_{2Me-H} characterize the extraction of the metals ^1Me and ^2Me, respectively, in relation to the concentration of hydrogen ions (for example under the effect of alkali); simultaneous solution of Equations (13) and (2) gives*

$$[^1MeR_2]_o[^2Me^{2+}]_A/[Me^{2+}]_A[^2MeR_3]_o = K_{1Me-H}/K_{2Me-H}; \tag{14}$$

$$K = K_{1Me-H}/K_{2Me-H}, \tag{15}$$

i. e., the constant of the exchange reaction of two metals with the same valence equals the ratio of the constants characterizing the extraction of each of these metals under the action of alkali. For example, the extraction of Zn and Co^{II} under the action of alkali obeys the equations (see Fig. 1):

$$\log\alpha_{Zn} = -10{,}0 + 2\,pH; \log\alpha_{Co} = -10{,}7 + 2\,pH. \tag{16}$$

Considering Equations (10, 11, and 13) and subtracting the second equation (16) from the first, we obtain $\log K_{Zn/Co} = 0.7$; $K_{Zn/Co} = 5.0$, where $K_{Zn/Co} = [ZnR_2]_o[Co^{2+}]_A/[Zn^{2+}]_A[CoR_2]_o$.

A study of the exchange reaction $(Zn^{2+})_A + (CoR_2)_O \rightleftharpoons (ZnR_2)_O + (Co^{2+})_A$ showed that the equilibrium constant was actually ~5. The given data show that the distribution of metal soaps and the related behavior of the metals in exchange extraction depend on the alkaline properties of the metals. The significance of the relation is explained in the following way. When the soaps are distributed, the aliphatic acid is distributed simultaneously between the phases. In the aqueous phase, the aliphatic acid is dissociated into ions to a very slight extent: $(HR)_A \rightleftharpoons (H^+)_A + (R^-)_A$, and $[H^+]_A[R^-]_A/[RH]_A = K_k \ll 1$, where K_k is the dissociation constant of the acid. Soap dissolved in the aqueous phase is practically completely dissociated: $(MeR_2)_A \rightleftharpoons (Me^{2+})_A + 2(R^-)_A$.

Considering that the water solubility of soaps of divalent metals is quite great [1] and that the dissociation constant of $C_7 - C_9$ aliphatic acids is small (of the order of 10^{-5}), one may assume that the concentration of R^- ions in the aqueous phase is determined only by the soap concentration: $(R^-)_A = 2(Me^{2+})_A$. Replacing, with some approximation, the activities by the concentrations and simultaneously solving the dissociation equation, with the expression for $(R^-)_A$ taken into account, we obtain

$$(Me^{2+})_A = K_a(HR)_A^2/2{\cdot}1/[H^+]_A; \quad \log(Me^{2+})_A = \log K_a(HR)_A^2/2 + pH. \tag{17}$$

The value of K_k we will take as that for enanthic acid: $K_k = 1.42 \cdot 10^{-5}$ [4]; according to our experimental data $(HR)_A = 0.062$ mole/liter. Substituting these values in (17) we have:

$$\log(Me^{2+})_A = -6{,}35 + pH \tag{18}$$

(the metal concentration is expressed in mole/liter).

Equation (18) is plotted on Fig. 2, which also gives the experimental points characterizing the distribution of Cu, Ni, and Co soaps. Equation (18) is obeyed with sufficient accuracy. It follows from Equation (17) and the

*In the case of metals of different valence the distribution coefficients depend on the hydrogen ion concentration to different degrees and as a result the separation coefficient depends on the hydrogen ion concentration: $\beta = (K_{1Me-H}/K_{2Me-H})[HR]^{m-n}/[H^+]^{m-n}$, where m and n are the valences of the first and second metals.

experimental data, as well, that as the soap concentration increases in the aqueous phase, the pH value increases. Of course, the soap concentration and, correspondingly, the pH cannot increase infinitely; the limit is set by the appearance of a solid phase, i. e., the solubility (activity) product of the corresponding metal hydroxide L:

$$[Me^{2+}][OH^-]^2 = L; \qquad [Me^{2+}]K_w^2/[H^+]^2 = L. \tag{19}$$

Replacing the activity $[Me^{2+}]$ by the concentration (Me^{2+}) and simultaneously solving (19) and (17), we obtain:

$$(Me^{2+})_{lim} = [K_x (HR)_A^2/2K_w]^{1/3} L^{1/3}, \tag{20}$$

where $(Me^{2+})_{lim}$ is the limiting value of the concentration of soap in water.

Thus, the solubility of the soap in the aqueous phase is proportional to the cube root of the solubility product of the metal hydroxide. This conclusion explains the relation between the behavior of a metal during its extraction with aliphatic acids and its alkalinity (an increase in "alkalinity" is characterized by an increase in the value of L). Exchange extraction of metals is an unusual hydrolytic method of extraction; it differs from the

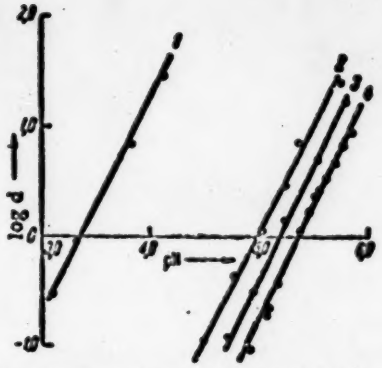

Fig. 1. Extraction of metals with aliphatic acids under the action of alkali: 1) Cu; 2) Zn; 3) Ni; 4) Co.

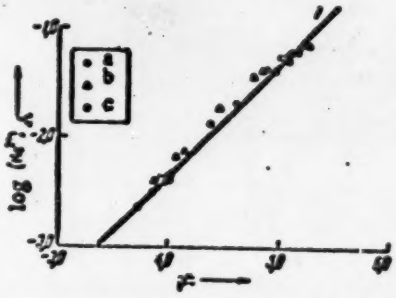

Fig. 2. The pH dependence of $\log(Me^{2+})_A$ in soap distribution. 1) line corresponding to Equation 18. Experimental points: a) Cu; b) Ni; c) Co.

usual hydrolytic method in that there are no precipitates. Of course, due to the absence of entrapment by the solid phase, the separation is more complete in this case. Furthermore, multistage separation in counter-current columns is readily accomplished. Thus, exchange extraction makes it possible to separate metals with similar properties (for example $Co^{II} - Ni^{II}$), which cannot be done by hydrolytic precipitation. At the same time, it is a method of extracting metals, for example, according to the reaction with alkali (Eq. 5-8).

In conclusion, we should note the unusual relation between the exchange extraction series of metals, as mentioned above, and the electrochemical series of metals. Metals to the right of a given one in the electrochemical series have a more positive normal potential and are usually characterized by lower alkalinity (a lower value of the solubility product of the hydroxide); they may be separated from the given metal by exchange extraction. More active metals, which are to the left in the electrochemical series, do not usually separate or separate to a small extent at the cathode during electrolysis of the given metal. Therefore, a combination of exchange extraction followed by electrolytic separation could be a method of obtaining pure metals in many cases. This procedure has been justified by the preparation of highly pure cobalt.

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THERMAL DECOMPOSITION OF ORGANIC COMPOUNDS OF PENTAVALENT ARSENIC

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(Presented by Academician A. E. Arbuzov, April 23, 1959).

In 1887 Crafts [1] found that when arsenic acid was heated to 220-230° in the presence of tetraethoxysilane, arsenous ester was formed. In 1947 Ya. F. Komissarov et al., [2] showed that esters of alkylarsinic acid isomerized into arsenous esters when heated. The corresponding alcohols were also isolated as reaction products.

Thermal decomposition of the oxides of (2-carboxyethyl)- and (2-carboxy-2-methylethyl) -diphenylarsine leads to the formation of bis-diphenylarsine oxide and a carboxylic acid [3]. It seemed interesting to us to study the pyrolysis of pentavalent arsenic compounds on the example of the following series: $AlkAs(O)(OAlk)_2$, $Alk_2As(O)OAlk$) and Alk_3AsO, where Alk = CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9. These substances were synthesized by oxidation of the corresponding trivalent arsenic derivatives. The compounds listed were pyrolyzed by heating at atmospheric pressure with distillation of the volatile products formed. Decomposition began at 200-220° in the reaction mass. Individual substances were isolated from the distillate by fractional distillation. Alkylarsinic

TABLE 1

Pyrolysis of Alkylarsinic Esters

Expt. No.	Starting ester	Substance obtained	B. p., °C/mm Hg	d_4^{20}	n_D^{20}	Yield, %*
1	n-$C_3H_7As(O)(OC_3H_7)_2$	n-$C_3H_7As(O)(OC_3H_7)_2$	121,5—124/11	1,2435	1,4520	40,7
		(n-$C_3H_7O)As(OC_3H_7)_2$	56—59/10	1,1623	1,4413	11,2
2	n-$C_3H_7As(O)(OC_3H_7$-n$)_2$	n-C_3H_7OH*				8,4
3	n-$C_3H_7As(O)(OC_4H_9$-n$)_2$	n-C_4H_9OH	115—117,5	0,8143	1,3972	17,1
		n-$C_3H_7As(OC_4H_9$-n$)_2$	111—115/12	1,0573	1,4528	5,7
		$As(OR)_3$**	121—125/11	—	1,4496	2,1
4	$CH_3As(O)(OC_4H_9$-n$)_2$	n-C_4H_9OH*	115,5—116	—	—	9,3
		$CH_3As(OC_4H_9$-n$)_2$	93—95/13	1,0846	1,4515	12,5
5	$C_2H_5As(O)(OC_4H_9$-n$)_2$	n-C_4H_9OH*	115,5—117	—	—	15,5
		$C_2H_5As(OC_4H_9$-n$)_2$	103—106/13	1,0727	1,4534	19,8

* Identified as the 3,5-dinitrobenzoate.

** Found %: As 26,62. $C_{12}H_{27}AsO_3$. Calculated %: As 26,74.

esters were obtained by oxidation of the corresponding alkylarsinous esters* with selenium dioxide [5, 6]. The alkylarsinic esters synthesized were apparently quite stable to the action of heat. Thus, when diethyl n-propylarsinate was heated, a considerable part of it was recovered unchanged. Therefore, the other alkylarsinic esters were heated so that the vapor temperature did not exceed 200°. The main arsenic-containing reaction product was then the corresponding alkylarsinous ester (Table 1). Its structure was confirmed by the fact that it formed alkyldiiodoarsine when treated with hydriodic acid. The formation of arsenous esters was observed in the pyrolysis of diethyl and di-n-butyl n-propylarsinates. In the second case, the isomerization product was similar in composition to the propyl ester of dibutylarsenous acid, but differed from the latter [7] in the n_D^{20} value. The pyrolyzate from di-n-butyl methylarsinate contained a carbonyl compound which reacted with 2,4-dinitrophenylhydrazine.

TABLE 2

Oxidation of Dialkylarsinous Esters with Selenium Dioxide

Expt. No.	Starting ester	Substances obtained	B. p., °C/mm Hg	d_4^{20}	n_D^{20}	Yield, %
1	$(C_2H_5)_2AsOC_2H_5$	$(C_2H_5)_2As(O)(OH$	m. p. 136—137°			1,5
		$(C_2H_5)_2AsOC_2H_5$	140—141	1,1148	1,4600	2,1
2	$(C_2H_5)_2AsOC_3H_7$-n	n-C_3H_7OH*				16,8
		$(C_2H_5)_2As(O)(OH)$	m. p. 135—137°			2,7
		$(C_2H_5)_2AsOC_3H_7$-n	54,5—57/13	1,0904	1,4621	0,2
3	$(C_2H_5)_2AsOC_4H_9$-n	$(C_2H_5)_2As(O)(OC_4H_9$-n)	130—130, 5/4	1,1922	1,4721	12,1
		$(C_2H_5)_2As(O)(OH)$	m.p. 136—137°			11,9
		$C_2H_5As(OC_4H_9$-n$)_2$	93,5—101/11		1,4522	2,0
4	$(CH_3)(n\text{-}C_4H_9)AsOC_2H_5$	$(CH_3)(n\text{-}C_4H_9)As(O)(OC_2H_5)$	110—111/2	1,2265	1,4729	26,0
		$(CH_3)(n\text{-}C_4H_9)As(O)(OH)$	m. p. 126—127°			11,1
5	$(CH_3)(n\text{-}C_4H_9)AsOC_4H_9$-n	n-C_4H_9OH	116—118			1,9
		$(CH_3)(n\text{-}C_4H_9)As(O)(OC_4H_9$-n)	133—134/3	1,1507	1,4676	24,9
		$(CH_3)(n\text{-}C_4H_9)As(O)(OH)$	m.p. 126—127°			5,5

*Identified as the 3,5-dinitrobenzoate.

From external appearances, the oxidation of dialkylarsinous esters proceeded similarly to that of alkylarsinous esters. However, a considerable part of the product was converted to tar in the first distillation and the consistency of the liquid changed. If the first distillation was carried out at a pressure of 13-15 mm Hg, only the starting material was isolated instead of the desired ester (Nos. 1, and 2, Table 2). Lowering the pressure to 4 mm made it possible to isolate the n-butyl ester of diethylarsinic acid. The yield of dialkylarsinic ester was increased if the solvent was removed in vacuum after the oxidation (Nos. 4 and 5, Table 2).

The distillate and tarry residue of the first distillation yielded, in addition to the dialkylarsinic ester, a series of products which were not observed in the synthesis of alkylarsinic esters. Thus, dialkylarsinic acids were formed in all cases and the alcohol with the radical of the alkoxy group of the starting compound in two cases (Nos. 2 and 5, Table 2). The oxidation products of the n-butyl ester of diethylarsinous acid yielded the di-n-butyl ester of ethylarsinous acid. The analogy between some oxidation products of dialkylarsinous esters and the thermal decomposition products of alkylarsinic esters gave us the idea that the dialkylarsinic esters formed during the oxidation may have been pyrolyzed during isolation. The pyrolysis of the n-butyl ester of methyl-n-butylarsinic acid confirmed this hypothesis: the pyrolyzate yielded butanol and the n-butyl ester of methyl n-butylarsinous acid and the presence of a carbonyl compound was detected (test with 2,4-dinitrophenylhydrazine). The case of the conversion $R_2As(O)(OR) \rightarrow R_2AsOR$ apparently may also explain the formation of arylarsinous esters [8] and arylalkylarsinous esters [9] during the action of alkyl halides on the silver salts of the corresponding arsinic acids.

*We reported the synthesis of alkylarsinous esters from alkyldiiodarsines and alcohols [4]. The esters obtained had iodine-containing impurities but were quite suitable for the synthesis of alkylarsinic esters.

The dialkylarsinous esters we obtained (Table 2) were viscous liquids with a weak, specific smell, which were readily hydrolyzed by water and atmospheric moisture. According to our calculations, the atomic refraction of arsenic equalled 8.19 in these compounds.

The dialkylarsinous esters were obtained by oxidation of trialkylarsines with hydrogen peroxide. Pyrolysis of trialkylarsine oxides (Table 3) yielded trialkylarsines and alcohols as the main products. In individual cases, the pyrolyzate yielded a small amount of the dialkylarsinous ester (Nos. 3 and 4, Table 3). The pyrolysis products of tri-n-propylarsine and methyl di-n-butylarsine oxides were shown to contain a carbonyl compound by reactions with 2,4-dinitrophenylhydrazine. In the latter case (No. 4, Table 3), the 2,4-dinitrophenylhydrazone was found to be identical with the 2,4-dinitrophenylhydrazone of butyraldehyde. Pyrolysis of trialkylarsine oxides was apparently accompanied by disproportionation of radicals as the pyrolyzate of methyldi-n-butylarsine yielded tri-n-butylarsine.

TABLE 3

Pyrolysis of Trialykylarsine Oxides

	Starting material	Substances obtained	B. p., °C/mm Hg	d_4^{20}	n_D^{20}	Yield, %
1	$(C_2H_5)_3AsO$	C_2H_5OH				2,9
		$(C_2H_5)_3As$	136—137	1,0750	1,4760	54,5
2	$(n\text{-}C_3H_7)_3AsO$	$n\text{-}C_3H_7OH$*				5,9
		$(n\text{-}C_3H_7)_3As$	74—76,5/10	1,0228	1,4750	35,8
3	$(CH_3)_2(n\text{-}C_4H_9)AsO$	$(CH_3)_2(n\text{-}C_4H_9)As$	133—135	1,0500	1,4673	23,7
		$(CH_3)(n\text{-}C_4H_9)_2AsC_4H_9\text{-}n$	83—85/11	—	1,4641	1,9
4	$(CH_3)(n\text{-}C_4H_9)_2AsO$	$n\text{-}C_3H_7CHO$**				3,9
		$n\text{-}C_4H_9OH$*				6,0
		$(CH_3)(n\text{-}C_4H_9)_2As$	75—76,5	1,0103	1,4724	14,9
		$n\text{-}C_4H_9)_3As$	114—116/10	0,0896	1,4716	2,5
		$(n\text{-}C_4H_9)_2AsOCH_3$	86—87,5/13	—	1,4685	0,8

*Identified as the 3,5-dinitrobenzoate.

**Identified as the 2,4-dinitrophenylhydrazone.

Thus in the cases we examined, the pyrolysis of pentavalent arsenic compounds proceeded in at least two directions: $RR'R''AsO \rightarrow R'R''AsOR$ (A) and $RR'R''AsO \rightarrow RR'R''As$ (B) (R is alkyl and R' and R'' are alkyl or alkoxy groups). The pyrolysis apparently yielded both compounds (A and B) in each case, but the isolation of individual products was hindered by the closeness of the boiling points of these substances. In addition to the products listed, the pyrolyzate contained alcohols and probably aldehydes. The analogy in both the conditions and the products of the pyrolysis indicate a single reaction mechanism.

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ADDITION OF TRICHLOROGERMANE TO ACETYLENE AND OLEFINS AND THEIR DERIVATIVES IN THE ABSENCE OF CATALYSTS

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Rochow et al., [1] were the first to add trichlorogermane to hexene-1 by prolonged boiling in the presence of benzoyl peroxide. They reported the formation of hexyltrichlorogermane in 22% yield. Without proving the order of addition, they assumed that in analogy with the addition of Cl_3SiH they had formed n-hexyltrichlorogermane.

Soon, trichlorogermane had been added to nine other olefins under the same conditions, namely, in sealed tubes at 85° [2]. Gilman and Gerow [3] added triphenylgermane to octadecene-1 also in the presence of benzoyl peroxide and established that n-octadecyltriphenylgermane was thus formed in 67% yield. It was demonstrated that the addition of triphenylgermane to triphenylallylgermane formed 1,3-bis-(triphenylgermyl)-propane, i.e., in this case, as well, triphenylgermyl addition occurred at the terminal carbon of the olefin radical. The authors reported that while the yield of the addition product reached 85% in the latter case, triphenylsilane was not added at all under analogous conditions. Lesbre and Satge [4], who recently synthesized organogermanium compounds with a functional group in the chain, showed that the addition of trialkylgermanes to allyl alcohol or acrolein required the presence of a catalyst (benzoyl or platinum peroxide), while their addition to acrylonitrile and acrylic acid or its esters proceeded without any catalysts on boiling under reflux.*

V. A. Ponomarenko and G. Ya. Vzenkova [6] added trichlorogermane to ethylene in the presence of H_2PtCl_6 in an autoclave; $C_2H_5GeCl_3$ was obtained in less than 25% yield under these conditions.

In the present investigation we found that without any catalysts and initiators, trichlorogermane added at the moment of contact (with the evolution of a large amount of heat) even at room temperature to olefins (1, 2) (from ethylene to octene-1), acetylene (3), acrylonitrile (4), allyl acetate (8), allyl chloride (5) and methallyl chloride (6) and even to vinyl chloride and β-chlorovinyltrichlorosilane (9, 10). The yields and properties of the compounds obtained are presented in Table 1.

It is interesting that the yields of the addition products were found to be higher than those given in the literature for addition in the presence of catalysts. As is known [7], the addition of silicochloroform to the substances given in Table 1 mainly occurs only in the presence of catalysts; in exceptional cases it also occurs under drastic conditions without catalysts. Thus, it is evident that in extremely different addition reactions, trichlorogermane is considerably more active than trichlorosilane.

EXPERIMENTAL

Trichlorogermane, $HGeCl_3$. Finely divided germanium (50 g), mixed with 10 g of precipitated copper, was placed in a glass tube (18 mm in diameter and 80 mm in length). The tube was heated to 450° and a fast

*We note the interesting fact that the French investigators stated that trimethylsilane was hardly added to methyl acrylate, even in the presence of catalysts (the nature of these was not indicated). This statement is not accurate. A. D. Petrov and S. I. Sadykh-Zade [5] showed that trialkylsilanes add to acrylic ester in the 1-4 position in the presence of H_2PtCl_6.

stream of hydrogen chloride passed through it. In a trap cooled with dry ice we collected 115 g of condensate, which yielded 93 g of a fraction with b. p. 77-78° on distillation. The yield was 79%, calculated on germanium. This fraction was a turbid liquid due to a small amount of some liquid compound of germanium emulsified in it. On standing, the liquid lightened somewhat and drops of the compound mentioned separated on the walls of the vessel. The $HGeCl_3$ was thus obtained and used in subsequent reactions.

γ-Cyanoethyltrichlorogermane, $Cl_3GeCH_2CH_2CN$. 18 g of $HGeCl_3$ was added with stirring to 5.3 g of acrylonitrile. The first drops of $HGeCl_3$ rapidly produced strong heat evolution. The rate of $HGeCl_3$ addition was such that the temperature did not rise above 60-70°. When all the $HGeCl_3$ had been added, the contents of

TABLE 1

Expt. No.	Unsaturated compound	Reaction products	B. p., °C (mm Hg)	M.p., °C	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield, %
1	$CH_2=CH_2$	$CH_2CH_2GeCl_3$	141.5(761)		1,4765	1,6091	38,36	38,55	88
2	$CH_2=(CH_2)_2CH=CH_2$	$CH_2(CH_2)_2GeCl_3$	190(93)		1,4720	1,2712	64,48	63,33	88
3	$CH\equiv CH$	$Cl_3GeCH_2CH_2GeCl_3$	130(12)	56					22
4	$CH_2=CHCN$	$Cl_3GeCH_2CH_2CN$	135(22)	37,7					53
5	$CH_2=CHCH_2Cl$	$Cl_3GeCH_2CH_2CH_2Cl$	105(20)		1,5070	1,6220	45,88	45,02	77,4
6	$CH_2=C(CH_3)-CH_2Cl$	$Cl_3GeCH_2CH(CH_3)CH_2Cl$	92(11)		1,5000	1,5759	50,49	49,65	58,8
7	$CH_2=CHSiCl_3$	$Cl_3GeCH_2CH_2SiCl_3$	120(15)	35					83
8	$CH_2=CHCH_2O_2CCH_3$	$Cl_3GeCH_2CH_2O_2CCH_3$	127,5(12)		1,4855	2,5092	52,15	51,21	69,8
9	$CH_2=CHCl$	$Cl_3GeCH_2CH_2Cl$	75(15)		1,5025	1,7615	41,05	40,35	32,8
10	$Cl_2SiCH=CHCl$	$Cl_3SiCH_2CHCl_2$	120(13)		1,5265	1,8350	62,98	62,54	68

the flask were vacuum distilled. We isolated 12.3 g of β-cyanoethyltrichlorogermane with b. p. 135° (22 mm). The yield was 53%.

$C_3H_4GeNCl_3$. Found %: Cl 45,71; 45,83. Calculated %: Cl 45,84

There was a residue of 4 g of polymer.

γ-Chloropropyltrichlorogermane, $Cl_3GeCH_2CH_2CH_2Cl$. 36 g of $HGeCl_3$ was added to 10.8 g of allyl chloride under analogous conditions. Vacuum distillation yielded 28 g of γ-chloropropyltrichlorogermane with b. p. 105° (20 mm). The yield was 77.4%.

$C_3H_6GeCl_4$. Found %: Cl 55,46; 55,53. Calculated %: Cl 55,29

γ-Chloroisobutyltrichlorogermane, $Cl_3CH_2CH(CH_3)CH_2Cl$. 36 g of $HGeCl_3$ was added to 12 g of methylallyl chloride under the same conditions. Vacuum distillation gave 21 g of γ-chloroisobutyltrichlorogermane with b. p. 90-93° (11 mm). The yield was 58.3%.

$C_4H_8GeCl_4$. Found %: C 17,88, 18,14; H 2,95; 3,28; Cl 52,48; 52,28. Calculated %: C 17,75; H 2,98; Cl 52,43

Here we also obtained 6 g of a product boiling at 148-153° (10 mm).

1-(Trichlorogermyl)-2-(trichlorosilyl)-ethane, $Cl_3SiCH_2CH_2GeCl_3$. 14 g of trichlorogermane was gradually added to 3 g of vinyltrichlorosilane. Vacuum distillation gave 15.6 g of $Cl_3SiCH_2CH_2GeCl_3$ with b. p. 120° C (15 mm). The yield was 83%.

$C_2H_4GeSiCl_6$. Found %: Cl 61,04; 61,84. Calculated %: Cl 62,28

1,2-Bis-(trichlorogermyl)-ethane, $Cl_3GeCH_2CH_2GeCl_3$. A stream of acetylene was passed through 18 g of trichlorogermane until the liquid, which first heated up strongly, cooled. Vacuum distillation gave 10.5 g of $Cl_3GeCH_2CH_2GeCl_3$ with b. p. 130-131° (12 mm). The yield was 90%.

Found %: Cl 55.43; 55.20
$C_2H_4Ge_2Cl_6$. Calculated %: Cl 55.12

There was a residue of 3 g of polymeric product.

Ethyltrichlorogermane, $C_2H_5GeCl_3$. Ethylene was bubbled through 18 g of trichlorogermane. The cooled liquid was distilled to give 11.5 g of ethyltrichlorogermane with b. p. 141.5° (761 mm). The yield was 55%.

A high-boiling fraction (2 g) remained.

n-Octyltrichlorogermane, $n\text{-}C_8H_{17}GeCl_3$. 18 g of $HGeCl_3$ was added to 11.2 g of octene-1. The liquid evolved heat, then cooled and was distilled to give 16 g of n-octyltrichlorogermane with b.p. 130° (13 mm). The yield was 55%.

γ-(Trichlorogermyl)-propyl acetate, $Cl_3GeCH_2CH_2CH_2 \cdot O_2CCH_3$. 45 g of $HGeCl_3$ was added to 17.5 g of allyl acetate. Vacuum distillation gave 20 g of γ-(trichlorogermyl)-propyl acetate with b. p. 127-128° (12 mm). The yield was 40.8%; there was a residue of 18 g of polymer.

Found %: C 21.70, 21.60; H 3.45, 3.49; Ge 26.09, 25.89; Cl 38.14, 38.32
$C_5H_9GeO_2Cl_3$. Calculated %: C 21.44; H 3.24; Ge 25.92; Cl 37.98.

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ABIENOL, ITS PREPARATION AND PROPERTIES

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(Presented by Academician B. A. Arbuzov, May 11, 1939)

In 1942, Winhaus and Mucke [1] isolated from the resin of Abies pectinata D. C. an alcohol with the general formula $C_{11}H_{22}O$, which they called abienol. With water, abienol formed a crystal hydrate, abienol hydrate with m. p. 62°. On hydrogenating abienol or abienol hydrate, they isolated dihydroabienol with m. p. 38°. A tetra nitromethane test on dihydroabienol gave a negative result; Winhaus and Mucke considered abienol to be a tertiary alcohol with one double bond. Formaldehyde, isolated on ozonolysis, indicated that the abienol molecule contained the $=CH_2$ grouping.

On investigating the chemical composition of pine resin of Abies sibirica Ldb [2], we detected abienol among the involatile components of the secretion and isolated it in the form of abienol hydrate, which corresponded in properties and analysis to abienol hydrate of Winhaus and Mucke (see Table 1).

TABLE 1

Name of compound	M. p., °C	$[\alpha]_D$ in ether, °	$[\alpha]_D$ in alcohol, °	n_D^{20}	λ_{max}, mμ	Source
Abienol hydrate	63—65	+19,5	+37,4	—	238 (log ε 4,18)	Our expt.
	62	+18,8	—	—	—	[1]
Abienol	40—42	—	+38,59	—	238 (log ε 4,18)	Our expt.
	—	+7,9	—	1,5328	—	[1]

However, the abienol we obtained from the abienol hydrate did not correspond in properties to the preparation of Winhaus and Mucke. It was a crystalline substance with m. p. 40-42° and with a considerably higher rotatory power. Contrary to the data in [1], abienol hydrate and abienol contained two double bonds. Depending on the length of the experiment, determination of the iodine number led to a gradual increase in the number up to the value corresponding to two double bonds. The first double bond was saturated by the second day, while saturation of the second required 7-8 days. Hydrogenation in the presence of platinum black in absolute alcohol or glacial acetic acid formed tetrahydroabienol, $C_{11}H_{22}O$, with m. p. 48-49° and $[\alpha]_d$ −4.0. Hydrogenation of the first double bond proceeded much more rapidly than hydrogenation of the second, indicating a difference in their character.

Analysis of the IR absorption spectra made it possible to arrive at more definite conclusions on the double bonds in the abienol hydrate molecule. The spectrum of the latter had two bands, corresponding to C = C valence oscillations: 1600 cm^{-1} and 1642 cm^{-1}. The presence of these bands may be explained by the existence of two conjugated double bonds in the abienol hydrate molecule. As is known [3], a diene has two bands in this region

with the band at 1600 cm^{-1} less intense than that at 1642 cm^{-1}, as we had in the ablenol hydrate spectrum. The presence of a conjugated system in the ablenol hydrate molecule was also confirmed by its ultraviolet spectrum, which contained an absorption band at 238 mμ (log ε 4.18). A narrow and quite intense band at 3100 cm^{-1} in the ablenol hydrate spectrum may be assigned to CH valence oscillations in a $=CH_2$ group [4]. This band disappeared completely during hydrogenation and polymerization. A weak band present at 1810 cm^{-1} (probably an overtone) is characteristic of vinyl compounds [5]. Hydrogenation and polymerization led to disappearance of this absorption band. It is very probable that ablenol hydrate contains the grouping $-CH=CH_2$. This is also supported by the presence of bands at 990 and 906 cm^{-1}, characteristic of CH deformation oscillations in the $-CH=CH_2$ group [5]. Polymerization and hydrogenation led to complete disappearance of the band at 990 cm^{-1} and the intensity of the band at 906 cm^{-1} was reduced to half. The second double bond was apparently tertiary – tertiary and was in an exocyclic position. This hypothesis was confirmed by the presence of a maximum of the absorption band at 238 mμ (calculated value for such a system, 237 mμ).

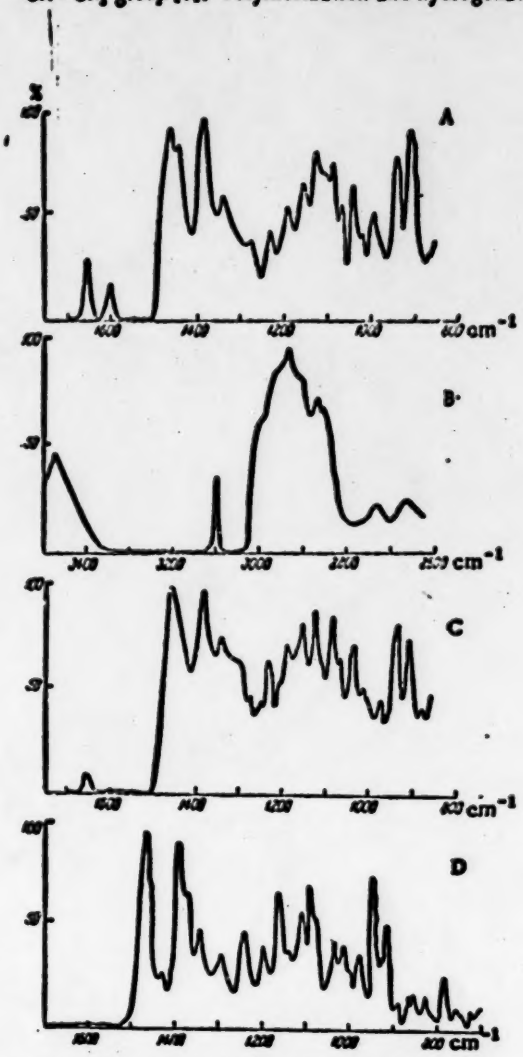

Fig. 1. IR spectra in 5% M CCl_4: A and B) ablenol hydrate; C) ablenol polymer; D) tetrahydroablenol. A, C, and D) layer thickness 208 μ, NaCl prism; B) layer thickness 108 μ, LiF prism.

The presence of very intense absorption bands in the IR spectra of ablenol hydrate, ablenol polymer and tetrahydroablenol at 1460 cm^{-1} and at 1384 cm^{-1}, which are caused by deformation oscillations in the CH_2 and CH_3 groups, indicates the presence of the latter in the ablenol hydrate molecule. We obtained similar results on analyzing the IR spectrum of ablenol. The spectrum also had absorption bands at 1597 cm^{-1} and 1643 cm^{-1}, characteristic of a conjugated system of double bonds. There were also bands at 905; 938; 1800; 1384; 1460 cm^{-1}.

As was stated above, the ablenol of Winhaus and Mucke had a considerably lower rotatory power than the ablenol we isolated. This was explained by the great instability of ablenol and its capacity for polymerization. If ablenol hydrate was heated to 90-95° in vacuum (3 mm Hg), it lost water (1 mole of H_2O) and changed to ablenol. Solution of the ablenol thus obtained in alcohol deposited a white, amorphous precipitate with m. p. 115-120°. Elementary analysis and a molecular weight determination showed that we had a polymer of ablenol, $(C_{17}H_{22}O)_x$ with $[\alpha]_D$ +5°. The polymerization of ablenol could not be produced by irradiation with visible light. We can now understand the contradictory data of Winhaus and Mucke. The latter were undoubtedly dealing with partially polymerized ablenol.

It should also be stated that, contrary to the data of Winhaus and Mucke, ablenol could be reconverted into ablenol hydrate if the ablenol was treated with ethyl alcohol (96%) and cooled normally. Thus, the change from ablenol hydrate to ablenol and back was not accompanied by structural changes in the molecule (excluding polymerization).

EXPERIMENTAL

Isolation of abienol hydrate. 1 kg of pine resin (constants: $[\alpha]_D - 10.88$, n_D^{19} 1.5153, d_4^{19} 1.0021, acid No. 68, sap. No. 119, iodine No. 154) was treated with ligroin (20 liters) until the solution was no longer turbid. The amorphous precipitate was collected by filtration and the excess ligroin removed. To 3-3.5 liters of ligroin solution was added 1 liter of diethyl ether. The solution obtained was treated with 10% aqueous potassium hydroxide. The acids then passed into the aqueous solution as salts. The ether-ligroin solution remaining after removal of the resin acids was used for isolating abienol hydrate. For this purpose, the ether was removed and the turpentine steam distilled to leave a viscous, yellowish mass, which was extracted with ether. The ether was then removed without the solution being heated and the residue was dissolved in ethyl alcohol. When the solution stood at -5 to -10°, it deposited needle-like crystals (50 g), which had the following constants after two recrystallizations from alcohol: m. p. 63-64°; $[\alpha]_C + 18.0°$, $[\alpha]_D + 19.5°$, $[\alpha]_F + 38.4°$, $[\alpha]_F/[\alpha]_C = 2.13°$ (C = 5, in ether); $[\alpha]_C + 30.0°$, $[\alpha]_D + 37.4°$, $[\alpha]_F + 66.0°$, $[\alpha]_F/[\alpha]_C = 2.20°$ (C = 5, in alcohol; 238 mμ (log ε 4.18).

Elementary analysis:

	Found %:	C 76.88; 77.01;	H 11.73; 11.85; number of act. H 2.7
$C_{11}H_{18}O_2$.	Calculated %:	C 76.62;	H 11.37; number of act. H 3

Iodine numbers of abienol hydrate: after a sample had stood with Houbly's solution for 1 day: 130.6, 132.3; 3 days: 150.4, 151.3, 8 days 185, 185.2 (calculated for two double bonds, 190).

Preparation of tetrahydroabienol by hydrogenation of abienol hydrate. We used 4.1 g of abienol hydrate, 60 ml of alcohol and 0.4 g of Pt black. 648 ml of H_2 was absorbed (calculated for two double bonds, 690 ml). Removal of the alcohol yielded a substance which melted at 45-46°. Recrystallization of this from acetic acid gave a product with m. p. 48-49°, $[\alpha]_D - 4.0$ (C = 3, in alcohol); d_4^{19} 0.93481, n_d^{19} 1.48778.

The same results were obtained by hydrogenating abienol hydrate in glacial acetic acid. Elementary analysis:

	Found %:	C 80.52; 80.58;	H 12.69; 12.78
$C_{11}H_{22}O$.	Calculated %:	C 80.88;	H 12.77

MR_D Found 77.63, Calculated 77.83.

Preparation of abienol. Into a column filled with 700 g of aluminum oxide (neutral, act. 3) was introduced 20 g of abienol hydrate, dissolved in 150 ml of ligroin. The column was washed with 1 liter of ligroin and the abienol eluted with 1 liter of benzene. The benzene was then removed in vacuum in a stream of nitrogen in the dark without heating. The last traces of benzene were removed in vacuum at a pressure of 0.1 mm Hg. After removal of all the benzene, the substance crystallized. We obtained 15 g of a crystalline product with m. p. 40-42°; $[\alpha]_D + 38.59°$ (C = 10, in alcohol); λ_{max} 238 mμ (in alcohol), log ε 4.31.

Elementary analysis:

	Found %:	C 82.45; 82.58;	H 11.86; 11.83; OH 6.33; 6.49
$C_{11}H_{20}O$.	Calculated %:	C 82.25;	H 11.37; OH 6.85

Preparation of abienol polymer. A sample of abienol hydrate (1.2564 g) was placed in a weighed tube and heated at 90-95° at a pressure of 3 mm for 5 hours. During this, 0.0847 g of water (6.74%) was liberated. The clear viscous mass obtained was dissolved in 10 ml of alcohol. The insoluble, white amorphous precipitate was collected and dried. We obtained 0.1 g of product with m. p. 115-120° and $[\alpha]_D = 5°$.

	Found %:	C 82.53; 82.44;	H 11.78; 11.76; M 1269; 1301
$(C_{11}H_{18}O)_3$.	Calculated %:	C 82.25;	H 11.37; M 1228.

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DETERMINATION OF ORGANOALUMINUM COMPOUNDS BY AN INDICATOR METHOD

Corresponding Member Acad. Sci. USSR, G. A. Razuvaev and A. I. Graevskii

Organoaluminum compounds have found wide application as catalysts in the polymerization of ethylene, propylene, and other α-olefins and, as a rule, they are used as dilute solutions (0.1-10%). The analysis of such solutions presents considerable difficulties and at the present time there is no rapid and simple method of analysis for these substances.

It may be supposed that the presence of an unfilled 3p electron level at the central aluminum atom, open to electronic attack, determines the acidic properties of organoaluminum compounds ("general acids" according to Lewis [1]) and makes it possible to titrate them in the presence of normal acid-base indicators.

In this connection it seemed interesting to determine how alkylaluminums and arylaluminums and their derivatives would interact with indicators and organic bases. For this purpose, $Al(C_2H_5)_3$ (b. p. 130°/50 mm), $Al(C_2H_5)_2Br$ (b. p. 148°/50 mm), $Al(C_2H_5)_2Cl$ (b. p. 125°/50 mm), $AlC_2H_5Cl_2$ (b. p. 115°/50 mm), $Al(C_2H_5)_2OC_6H_5$ (b. p. 109°/10 mm), $AlC_2H_5(OC_2H_5)_2$ (b. p. 148°/10 mm), which were synthesized by known methods, and also $Al(C_6H_5)_3$ and $Al(C_4H_9)_3$* were dissolved in purified toluene, that had been freed from oxygen, and mixed with dichloroethane solutions of methyl violet.

It was observed that when $Al(C_2H_5)_3$ and its halo derivatives were added, the indicator changed color from violet (alkaline form) to yellow or green (acid form). $Al(C_6H_5)_3$ and $Al(C_4H_9)_3$ acted on the indicator analogously.

If excess of any organic base was added to the yellow or green solutions, the color again became violet. It is interesting that compounds of the type AlR_2OR and $AlR(OR)_2$ did not change the color of the indicator.

The neutral properties of these substances can probably be explained by shielding of the 3p level of aluminum by the free electron doublets of oxygen.

We titrated organoaluminum compounds with certain organic bases (butyl acetate, ethyl acetate, dimethylaniline, ethyl ether, pyridine etc.), using indicators. Indicators were chosen which were readily soluble in organic solvents and gave clear changes at the equivalence point. As a rule, they contained amino groups (methyl violet, crystal violet, gentian violet etc.).

Figure 1 (a, b, c, and d) shows the titration curves of $Al(C_6H_5)_3$ and $Al(C_2H_5)_2Cl$, $AlC_2H_5Cl_2$, a sesquichloride (an equimolecular mixture of $Al(C_2H_5)_2Cl + AlC_2H_5Cl_2$) and $Al(C_2H_5)_2Br$ with dimethylaniline in toluene in the presence of methyl violet. The molar ratio of dimethylaniline : organometal compound is plotted along the abscissa and the percent of the alkaline form of the indicator along the ordinate. The percent of the alkaline form was determined spectrophotometrically on a UM-2 monochromator. The results obtained lead to the following conclusions:

1. The titration curves of organoaluminum compounds with organic bases are similar to the titration curves of strong acids with strong bases. Alkylaluminums and arylaluminums and their derivatives are quite strong aprotonic acids.

* $Al(C_4H_9)_3$ was kindly presented to us by A. F. Popov and $Al(C_6H_5)_3$, by E. V. Mitrofanova.

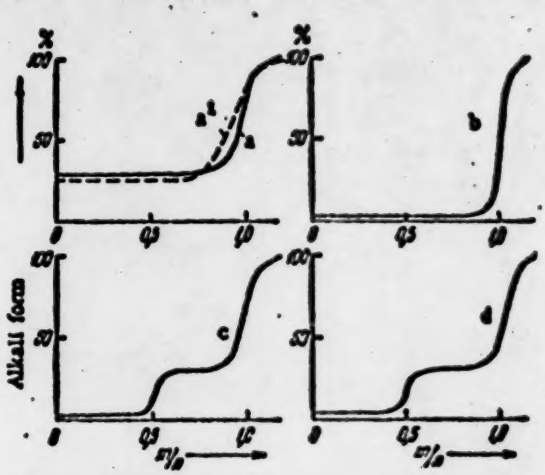

Fig. 1. Titration of organoaluminum compounds with dimethylaniline in the presence of methyl violet. a) $Al(C_2H_5)_3$; a' – $Al(C_2H_5)_2Cl$; b) $AlC_2H_5Cl_2$; c) $Al(C_2H_5)_2Cl + AlC_2H_5Cl_2$; d) $Al(C_2H_5)_2Br$.

2. Dimethylaniline reacts with these acids in a 1:1 ratio.

3. $Al(C_2H_5)_2Br$ and $AlC_2H_5Cl_2$ differ considerably in strength from $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Br$.

4. $Al(C_2H_5)_2Br$ behaves as a dibasic acid and as yet, no satisfactory explanation can be found for this.

5. It is possible to determine $Al(C_2H_5)_2Cl$ and $AlC_2H_5Cl_2$ separately in mixtures of them.

To compare the strength of the acids in the series $Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $AlC_2H_5Cl_2$, $Al(C_2H_5)_2Br$ we used the so-called indicator salt stability method [2]. It is based on the fact that a salt formed by a given base with any acid decomposes in solution (undergoes solvolysis) the more completely and at a higher concentration, the weaker the acid. If an indicator is taken as the base, then the decomposition of its salt can be conveniently assessed from the change in color. Thus, methyl violet has a violet color in the free state. Its salts with acids are yellow or green. On dilution of the salt solution, the equilibrium of the reaction

$$\underset{\text{yellow}}{\text{Ind A}} \rightleftharpoons \underset{\text{violet}}{\text{Ind}} + \text{A}, \qquad (1)$$

where A, the acid, is displaced to the right and the salt decomposes completely at a definite dilution (the color becomes violet).

Table 1 gives comparative data on the dilution of solutions of salts of methyl violet with triethylaluminum and its halogen derivatives (dilution required for complete decomposition of the triethylaluminum salt taken as unity). We also give the values of the relative electroconductivity of the acids compared (electroconductivity of $Al(C_2H_5)_3$ taken as unity). As can be seen from the data in Table 1, there is a parallel between the results obtained by the dilution method and electrochemical data. According to these results, the acids may be arranged in the following order with respect to strengths

$$Al(C_2H_5)_3 < Al(C_2H_5)_2Cl < Al(C_2H_5)_2Br < AlC_2H_5Cl_2.$$

It should be noted that only dilute solutions of alkylaluminums can be used with indicators. Solutions with concentrations above 30-40% usually destroy the indicator. Toluene, xylene, ligroin and heptane are used as solvents.

TABLE 1

Experiment on Decomposition of Indicator Salts

Acid	Dilution*	Electro-conductivity**
$Al(C_2H_5)_3$	1	1
$Al(C_2H_5)_2Cl$	15	9
$Al(C_2H_5)_2Br$	120	48
$AlC_2H_5Cl_2$	855	85

* The dilution at which the salt formed between triethylaluminum and methyl violet decomposed was arbitrarily taken as unity.

** The electroconductivity of triethylaluminum solution was taken as unity.

The present work is of practical interest for rapid determination of the concentration of organoaluminum compounds in the presence of their oxidation products of the type AlR_2OR and $AlR(OR)_2$. Organoaluminum compounds can also be detected qualitatively by means of acid-base indicators (in the absence of other acids, of course).

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POSSIBILITY OF PREPARING POLYMERIC MATERIALS WITH SEMICONDUCTOR PROPERTIES BASED ON POLYACRYLONITRILE

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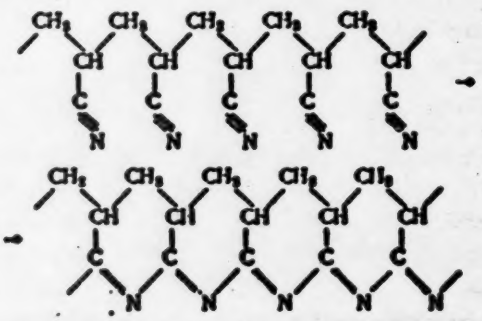
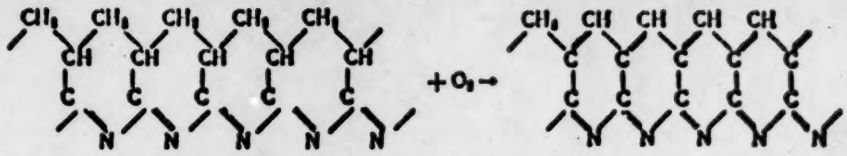
The difficulty of producing organic materials with electron conductivity is connected with the fact that due to the characteristics of normal organic compounds, permitted energy zones, if they are formed at all, are narrow and the forbidden zones are very wide. The width of the forbidden zones of such substances is so great that electron excitation does not occur at temperatures below the decomposition point. The semiconductor properties of organic substances described in the literature are usually connected with the presence of condensed aromatic rings and N atoms. Possibly valuable polymers are those with multiple, and especially conjugated double bonds, which also contain in the chain atoms with electrons in the outer levels that do not participate in a chemical bond (for example, nitrogen atoms). In such a polymer, current carriers must arise comparatively readily and with sufficiently high regularity in the polymer structure; the separation between the electrons in them must be small. The required degree of regularity may be assessed approximately from the free path length of an electron in a semiconductor, the length of a C–C bond, the length of the monomer unit, and the electron wavelength. It was found that in the case of a maximally stretched fiber in which the polymer molecules are oriented in the direction of the current, so that there would not be scattering at structural irregularities caused by the irregularity of the formation, it is sufficient to have a polymer molecule whose basic chain does not contain branchings consisting of more than 12 carbon atoms to each 35 monomer units. It is quite possible to build up polymers of such a degree of regularity at the present time.

From the point of view presented, it was of considerable interest to study the thermal conversion products of polyacrylonitrile, which have only been investigated up to now from the point of their considerable thermal stability [5].

It has been suggested that polyacrylonitrile undergoes the following conversions during thermal treatment [2]:



and then due to oxidative dehydrogenation



The presence of conjugated double bonds and also regularly alternating nitrogen atoms, whose electron pairs do not form chemical bonds and are acted upon by both vinyl (relative to the nitrogen atom) and allyl double bonds, leads one to expect that these polymers will have semiconductor properties.

We investigated the semiconductor properties of the thermal conversion products of polyacrylonitrile, obtained by polymerization of acrylonitrile with organometallic catalysts (LiC_4H_9), at low temperatures (mol. weight 10,000), with lithium in liquid ammonia and by oxidation-reduction initiation (mol. weight 100,000), and also a

TABLE 1

Preparation method	Treatment		E. p. r. data			Number of electrons with unpaired spins in 1 g of substance
	thermal	irradiation	ΔH, gauss	g-factor	Δg	
Oxidation-reduction initiation	–	–	No signal			
The same	+	–	31.7	1.981	–0.021	$4.0 \cdot 10^{18}$
Radiation polymerization	–	–	No signal			
The same	+	–	28.2	1.998	–0.004	$5.1 \cdot 10^{18}$
Ionic polymerization (t = –70°)	–	–	No signal			
The same	–	+	No signal			
" "	+	–	25.7	1.989	–0.013	$1.7 \cdot 10^{18}$
" "	+	+	24.9	2.001	–0.001	$1.5 \cdot 10^{19}$

polymer obtained by ionic polymerization with subsequent irradiation with a γ-ray dose of $1.1 \cdot 10^{22}$ ev. Polyacrylonitrile samples were subjected to thermal treatment both as powders and as samples in the form of fibers. The samples obtained were investigated by means of electron paramagnetic resonance (e. p. r); the temperature dependence of electroconductivity was determined for some samples of fibers. The e.p.r. apparatus and the measurement procedure have been described [3]; all the e.p.r. spectral measurements (see Table 1) were carried out at room temperature.

From the data in Table 1 it follows that:

1. The semiconductors obtained have electron conductivity ($\Delta g < 0$).
2. The concentration of current carriers is 10^{18}-10^{19}, i.e., degeneration is small.
3. The half-width of the band of the e.p.r. spectra, characterizing the relaxation time, equals 10-20 gauss.

No hyperfine structure in the e. p. r. spectrum was noted in any case and only one relatively narrow line was observed in accordance with the results of Fletcher [4].

Figure 1 shows the temperature dependence of electroconductivity for polyacrylonitrile obtained by oxidation-reduction initiation and subjected to thermal conversion.

The width of the forbidden zone, ΔE, calculated on the basis of the curve in Fig. 1, was found to be 1.7 ev. This semiconductor may work at a considerably higher temperature (the polymer still does not decompose at 300°) than germanium, for example. This forbidden zone width also indicates that the semiconductor properties are not connected with carbonization of the polyacrylonitrile samples during thermal treatment since the forbidden zone for graphite is extremely narrow. Thermally treated polyacrylonitrile decomposes hydrogen peroxide, which is characteristic of semiconductor catalysts.

TABLE 2

Method of preparing polyacrylonitrile	Treatment		E. p. r. data			Number of electrons with unpaired spins in 1 g of substance
	thermal	impregnation with salts	ΔH, gauss	g-factor	Δg	
Oxidation-reduction initiation	–	–	No signal			
The same	+	–	31.7	1.981	−0.021	$4.0 \cdot 10^{19}$
" "	+	$CrCl_3$	30.9	1.999	−0.003	$5.2 \cdot 10^{18}$
" "	+	$CuCl_2$	47.5	1.995	−0.007	$1.8 \cdot 10^{19}$
Ionic polymerization	–	–	No signal			
The same	+	$ZnCl_2$	26.4	2.000	−0.002	$8.8 \cdot 10^{18}$

Thus, the materials obtained on the basis of polyacrylonitrile have typical semiconductor properties and due to their character and high thermal stability, they may operate at elevated temperatures.

Since polyacrylonitrile swells in concentrated salt solutions, it is possible (before thermal treatment) to introduce into the polymer metal ions, which can then be electron donors.

Table 2 gives data obtained by studying the e. p. r. spectra of two samples of polyacrylonitrile impregnated with salt solutions before thermal treatment. The specific electroconductivity of a sample impregnated with $CuCl_2$ increased sharply and reached (at 300°) 10^{-2} $ohm^{-1} \cdot cm^{-1}$.

We also showed that preliminary irradiation of polyacrylonitrile with a γ-ray dose of $1.1 \cdot 10^{23}$ ev with subsequent thermal treatment led to a sharp increase in the concentration of electrons with unpaired spins (up to $1.5 \cdot 10^{19}$) in comparison with the unirradiated polymer. If the polyacrylonitrile was obtained by radiation polymerization and then treated thermally, the concentration of current carriers was practically the same as in samples obtained by normal methods of polymerizing acrylonitrile.

Thus, the action of γ-radiation on the polymer makes subsequent thermal treatment more effective in the preparation of materials with semiconductor properties.

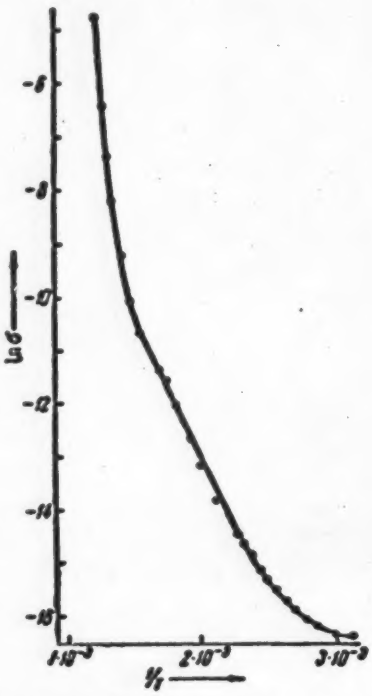


Fig. 1.

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ADDITION OF HYDROGEN BROMIDE TO 1, 1, 1, 2-TETRACHLOROPROPENE-2 AND 1,1,2-TRICHLOROPROPENE-2 IN THE PRESENCE OF BENZOYL PEROXIDE

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In previous work by us [1, 2] and in cooperation with L. I. Zakharkin [3] and A. B. Belyavskii [4], rearrangements were detected in free radicals of the types

$$R^1CCl_2-\dot{C}R''-{}^{\bullet}CH_2X\rightarrow R^1\dot{C}Cl-CClR''-CH_2X,$$

where R^1 = Cl or H, R'' = H, CH_3, Br, and X = Br, CCl_3, Cl, obtained in the addition of HBr, $BrCCl_3$ and Br_2 to polychloroolefins $R^1CCl_2CR''=CH_2$.

In the present work we studied the addition of HBr to 1,1,1,2-tetrachloropropene-2 and 1,1,2-trichloropropene-2 in the presence of benzoyl peroxide.

The interaction of HBr with 1,1,1,2-tetrachloropropene-2 led to a mixture of products, from which we isolated 1,1,2,2-tetrachloro-3-bromopropane (I) in about 30% yield. In addition, the reaction mixture contained $CHCl_2-CCl_2-CH_2Cl$ (II), $CCl_2=CCl-CH_2Br$ (III), $CCl_2=CCl-CH_2Cl$ (IV).

The presence of I and II shows that in this case also, the addition proceeded with a rearrangement of the type indicated. The small yield of I and also the presence of II, III and IV in the reaction products is apparently explained by the relatively low stability of the intermediate radicals, which decompose with the transfer of a chlorine atom:

$$CCl_3-CCl=CH_2+Br\rightarrow CCl_3\dot{C}Cl-CH_2Br\rightarrow \dot{C}Cl_2-CCl_2-CH_2Br$$

$$\dot{C}Cl_2-CCl_2-CH_2Br\begin{cases}\xrightarrow{+HBr} HCCl_2-CCl_2-CH_2Br+Br \\ (I)\\ \xrightarrow{+CCl_2CCl-CH_2} CCl_2=CCl-CH_2Br+CCl_3-\dot{C}Cl-CH_2Cl \\ (III)\end{cases}$$

$$CCl_3\dot{C}Cl-CH_2Cl\rightarrow \dot{C}Cl_2-CCl_2-CH_2Cl$$

$$\dot{C}Cl_2-CCl_2-CH_2Cl\begin{cases}\xrightarrow{+HBr} HCCl_2-CCl_2-CH_2Cl+Br \\ (II)\\ \xrightarrow{+CCl_2CCl-CH_2} CCl_2=CCl-CH_2Cl^{*}+CCl_3\dot{C}Cl-CH_2Cl \text{ etc.} \\ (IV)\end{cases}$$

According to composition, constants, and IR spectrum, substance I was identical with 1,1,2,2-tetrachloro-3-bromopropane, which we obtained by the scheme

$$CHCl=CCl-CH_2Cl\xrightarrow{NaBr}CHCl=CCl-CH_2Br\xrightarrow{Cl_2}CHCl_2-CCl_2-CH_2Br.$$

*It is possible that $CCl_2=CCl-CH_2Cl$ was formed as a result of allyl isomerization of $CCl_3CCl=CH_2$ under the action of hydrogen bromide.

and differed in constants and IR spectrum from 1,1,1,2-tetrachloro-3-bromopropane, which we obtained by chlorination of $CCl_3 = CH - CH_2Br$. When treated with alkali in ethyl cellosolve, (I) lost hydrogen chloride to form compound III, which was characterized as the hydrochloride of the diethylamino derivative $CCl_2 = CCl - CH_2N(C_2H_5)_2 \cdot HCl$ (V). According to composition, constants, and IR spectrum, compound II corresponded to 1,1,2,2,3-pentachloropropane, which was obtained synthetically by chlorination of $CHCl_2CCl = CH_2$. With diethylamine and thiourea, trichlorobromopropene II gave derivatives which were identified as the hydrochloride and picrate, respectively. On reaction with Hg, compound III gave a trichloroallylmercury bromide, $CCl_2 = CCl - CH_2HgBr$, identical with that obtained by an authentic method [5]. In properties, tetrachloropropene IV corresponded to known 1,1,2,3-tetrachloropropene and gave the corresponding derivative V with diethylamine.

The addition of HBr to 1,1,2-trichloropropene-2 proceeded without rearrangement to form 1,2-trichloro-3-bromopropane as can be seen from the scheme.

$$HCCl_2 - CCl = CH_2 + HBr \rightarrow [HCCl_2 - \dot{C}Cl_2 - CH_2Br] \xrightarrow{HBr} HCCl_2 - CHCl - CH_2Br.$$
$$\text{A} \qquad\qquad \text{(VI)}$$

This reaction course is evidently due to the great stability of the radical A formed in comparison with the radical with the structure $CHClCCl_2CH_2Br$, which could be formed by rearrangement.

According to composition, constants, and IR spectrum, substance VI was identical with known 1,1,2-trichloro-3-bromopropane. In addition, we obtained the isothiourea derivative $CHCl_2 - CHCl - CH_2SC(NH)NH_2$, in the form of the picrate, which was identical with the corresponding derivative synthesized from known 1,1,2-trichloro-3-bromopropane.

EXPERIMENTAL

Addition of HBr to $CCl_3CCl = CH_2$. Hydrogen bromide was passed at 60-70° through a solution of 120 g of 1,1,1,2-tetrachloropropene-2* and 0.5 g of benzoyl peroxide till saturation. The reaction products were washed with sodium carbonate solution and water and dried over $CaCl_2$; distillation on a column at 7 mm yielded the following fractions: I 26-27°, 17 g; II 27-57°, 6.5 g; III 57-77°, 46.5 g; IV 77-78°, 48 g, residue 15 g. Fraction I was original 1,1,1,2-tetrachloropropene-2.

Fraction II yielded 1,1,2,3-tetrachloropropene-1 with b. p. 70°/32 mm; n_D^{20} 1.5182; d_4^{20} 1.3500 (literature data [6]: b. p. 68°/30 mm; n_D^{20} 1.5160; d_4^{20} 1.3409). The hydrochloride of the diethylamino derivative had m. p. 168-169° (literature data [7]: 169°). A mixed melting point of the hydrochloride with the authentic compound was not depressed.

Fraction III consisted mainly of 1,1,2-trichloro-3-bromopropene-1 (18 g) and 1,1,2,2,3-pentachloropropane (16 g), which were isolated from the mixture by distillation on a column. Trichlorobromopropane (a strong lachrimator): b. p. 79-80°/20 mm; n_D^{20} 1.5488; d_4^{20} 1.7924 (literature data [1] for $CCl_2 = CCl - CH_2Br$ 78-79°/19 mm; n_D^{20} 1.5550; d_4^{20} 1.8835). The low constants are caused by the presence of close boiling fractions. The structure of the trichlorobromopropene was confirmed by preparation of the derivatives:

1) with diethylamine: m. p. of hydrochloride 169° (literature data [7] 169°);

2) with thiourea: m. p. of picrate 176-176.5° (from alcohol).

Found %: C 26.73; 26.88; H 1.72; 1.80
$C_{13}H_8Cl_3N_5O_7S$. Calculated %: C 26.77; H 1.80

3. with mercury: $CCl_2 = CCl - CH_2HgBr$, m. p. 117° (literature data [5]: m. p. 117°). Mixed melting points of the derivatives obtained with authentic samples were not depressed.

After treatment with an alcohol solution of thiourea and then H_2SO_4 in the cold to remove unsaturated compounds, 1,1,2,2,3-pentachloropropane was redistilled. B. p. 82°/20 mm; n_D^{20} 1.5122; d_4^{20} 1.6240; MR 39.93; Calculated MR 40.39.

Found %: C 17.02; 17.01; H 1.33; 1.34
$C_3H_3Cl_5$. Calculated %: C 16.65; H 1.40.

*See [6] for the preparation of 1,1,1,2-tetrachloropropene-2.

1,1,2,2,3-Pentachloropropane, obtained by chlorination of 1,1,2-trichloropropene-2, had b. p. 80°/19 mm; n_D^{20} 1.5100; d_4^{20} 1.6243; d_4^{23} 1.6190; MR 39.90; Calculated MR 40.39 (literature data [6]: b. p. 78-79°/16 mm; n_D^{20} 1.5080, d_4^{23} 1.6199).

The IR spectra of the pentachloropropanes obtained by the two methods were identical. The alternative, 1,1,1,2,3-pentachloropropane, has [6] b. p. 64-65°/9 mm; n_D^{20} 1.5105; d_4^{20} 1.6117, and also differs sharply in IR spectrum. Fraction IV consisted of 1,1,2,2-tetrachloro-3-bromopropane with b. p. 78°/7 mm; n_D^{20} 1.5385; d_4^{20} 1.9144; MR 42.71; calculated MR 43.29.

Found %: C 14.18; 14.06; H 0.98; 1.10; Hal 84.64; 84.68
$C_3H_2Cl_4Br$. Calculated %: C 13.81; H 1.16; Hal 85.00.

1,1,2,2-Tetrachloro-3-bromopropane was also obtained by chlorination of 1,2-dichloro-3-bromopropene-1* and had b. p. 78°/7 mm; n_D^{20} 1.5388; d_4^{20} 1.9109; MR 42.74; Calculated MR 43.29. The IR spectra of the 1,1,2,2-tetrachloro-3-bromopropanes obtained by the two methods were identical.

In addition, by chlorination of $CCl_2 = CH - CH_2Br$ we obtained 1,1,1,2-tetrachloro-3-bromopropane: b. p. 82-82.5°/8 mm; n_D^{23} 1.5347; d_4^{20} 1.8922; MR 42.89; Calculated MR 43.29.

Found %: C 13.94; 13.81; H 1.18; 1.19
$C_3H_2Cl_4Br$. Calculated %: C 13.81; H 1.16

The IR spectrum of this tetrachlorobromopropane differed noticeably from that of 1,1,2,2-tetrachloro-3-bromopropane.

The tetrachlorobromopropane isolated from fraction IV was dehydrochlorinated with alcoholic alkali to yield 1,1,2-trichloro-3-bromopropene with b. p. 76-78°/15 mm; n_D^{20} 1.5450; d_4^{20} 1.6775 (literature data [1] b. p. 78-79°/19 mm; n_D^{20} 1.5550; d_4^{20} 1.6835), which reacted with diethylamine to give a derivative, identical in constants with an authentic sample [1]. A mixed melting point of the hydrochlorides of these amines was not depressed.

Addition of HBr to $CHCl_2CCl = CH_2$. Hydrogen bromide was passed into a solution of 80 g $CHCl_2$-$CCl = CH_2$** and 0.5 g of benzoyl peroxide in 140 g of CCl_4 till saturation. The reaction product was treated as in the reaction with 1,1,1,2-tetrachloropropene-2 and after removal of the CCl_4 and the unreacted trichloropropene, it was distilled on a column. We isolated 27 g of a fraction with b. p. 64-65.5°/5 mm and 17 g of high-boiling fractions (125-135°/3 mm), which were not investigated more closely.

The fraction with b. p. 64-64.5°/5 mm was pure 1,1,2-trichloro-3-bromopropane; n_D^{20} 1.5303; d_4^{20} 1.8398; MR 38.02; Calculated MR 38.42. (1,1,2-Trichloro-3-bromopropane, obtained by the procedure in [3], had the following constants: b. p. 64-65°/5 mm; n_D^{20} 1.5296; d_4^{20} 1.8424).

Found %: C 16.03; 15.95; H 1.51; 1.58
$C_3H_4Cl_3Br$. Calculated %: C 15.92; H 1.78

The IR spectrum was identical with that of authentic 1,1,2-trichloro-3-bromopropane. We obtained the isothiourea derivative; m. p. of picrate 158.5°.

Found %: C 26.41; 26.31; H 2.36; 2.47
$C_{10}H_{10}Cl_3N_5O_7S$. Calculated %: C 26.65; H 2.24

A mixed melting point with the picrate of the isothiourea derivative obtained from authentic 1,1,2-trichloro-3-bromopropane was not depressed.

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*1,2-Dichloro-3-bromopropene was obtained by prolonged heating of 1,2,3-trichloropropene-1 with sodium bromide in acetone. B. p. 57-58°/17 mm; n_D^{20} 1.5438; d_4^{20} 1.8012; MR 33.27; Calculated MR 33.09

Found %: C 18.91; 18.91; H 1.47; 1.51
$C_3H_3Cl_2Br$. Calculated %: C 19.01; H 1.60.

**See [3] for the preparation of $CHCl_2 - CCl = CH_2$.

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ORGANOZINC COMPOUNDS OF THE CLASS Ar_2Zn AND THEIR DIOXANATES

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As we showed earlier for the first time [1], organozinc compounds of the class RZnX (X is a halogen) may be isolated in a pure, crystalline state as their complexes with ether or dioxane.*

It was reported in the literature that all the halides of zinc give corresponding dioxanates with the formula $ZnX_2 \cdot 2C_4H_8O_2$, while the ether, $ZnX_2 \cdot 2$ eth, is only known for zinc iodide [2].

In the light of these data it was interesting to determine whether analogous complexes exist for organozinc compounds of the class Ar_2Zn, the more so because previously, such a complex, for example, di-p-chlorophenylzinc with ether was not detected [3].

Actually, none of the diarylzincs described in the present work gave corresponding esterates, but in the case of dioxane,** we isolated the complexes $(C_6H_5)_2Zn \cdot C_4H_8O_2$ $(p\text{-}ClCH_2CH_2C_6H_4)_2Zn \cdot C_4H_8O_2$, $(\alpha\text{-}C_{10}H_7)_2ZnC_4H_8O_2$.

The dioxanates were white crystalline substances, which dissolved in ether and dioxane, but were insoluble in benzene and ligroin.

In connection with the preparation of the dioxanates (and also compounds of the class ArZnX [1]), it was necessary to improve the method for preparing the starting diarylzincs. The latter were first obtained by Hilpert and Gruttner [5] by heating diphenylmercury with metallic zinc in the absence of solvent.

This method, which is too drastic, was improved by Kocheshkov, Nesmeyanov and Potrosov [3], who carried out the reaction in boiling xylene and this made it possible to extend the synthesis to a series of organozinc compounds with substituents in the nucleus. A drawback to the method with zinc was the fact that the success of the synthesis depended on the state of the metal (so-called "Zink-Wolle" was preferable).

Later, Wittig [6] successfully used the reaction between zinc chloride and phenyllithium in an ether medium to synthesize diphenylzinc. After evaporation of the ether, the reaction product was distilled in high vacuum (0.01 mm, 160°).

To avoid the vacuum distillation, which would require a higher vacuum and an even higher temperature on going to higher diarylzincs (with this method, contamination by higher diaryls of the diphenyl type is unavoidable), we chose to work with solid aryllithiums.

The latter, obtained by the procedure developed by Talalaeva and Kocheshkov [7] (an X – M exchange reaction), in contrast to those prepared in the usual way with aryl bromide and metallic lithium in ether, contained hardly any diaryls (or, if necessary, the traces could be washed from them). Under our conditions, an insignificant amount of diaryls was produced in the reaction.

$$2ArLi + ZnX_2 \rightarrow Ar_2Zn + 2LiX \qquad (1)$$

* By crystallizing ethylzinc iodide from ethyl iodide, S. Gvozdov did not obtain the former in a pure state [4]. However, we were able to isolate a preparation corresponding to the formula C_2H_5ZnI according to analysis.

** 1,4-Dioxane everywhere.

The pure diarylzinc was therefore isolated easily by crystallization without distillation.

In this way, we were able to obtain diphenylzinc (83% yield), di-o-tolylzinc (71%), di-p-tolylzinc (45%) and di-α-naphthylzinc (46%) (the last two for the first time*

Solution of the diarylzincs in dioxane and removal of the bulk of the solvent yielded white, crystalline precipitates of the corresponding dioxanates.

The dioxanates were white, crystalline substances, which were soluble in ether and dioxane, in benzene on heating and insoluble in ligroin and hexane.

EXPERIMENTAL

All experiments were carried out in a special apparatus for work in an inert gas, which was previously developed in our laboratory [7]. The solid diarylilithiums were obtained according to [7] and analyzed for the ArLi content (there was usually a trace of lithium bromide). The figures presented later are calculated for pure ArLi.

Diphenylzinc from crystalline phenyllithium. Into a round-bottomed flask, fitted with a stirrer with a mercury seal, a reflux condenser, a dropping funnel, a thermometer, and a nitrogen inlet and first filled with pure, dry nitrogen, were placed 18.8 g (2 moles) of solid phenyllithium, 14.8 g (0.98 mole) of anhydrous zinc chloride, rapidly ground to a powder in a chamber under dry argon, and 150 ml of dry xylene. The stirrer was started and 30 ml of ether added from the dropping funnel (due to the insolubility of phenyllithium and zinc chloride in xylene). The temperature spontaneously rose to 60-80°. The mixture was then heated at the boiling point of xylene for 5-5.5 hours and the hot solution (70-80°) filtered free from lithium halide salts (glass filter No. 4). The residue on the filter was washed 2-3 times with hot xylene, the bulk of the solvent removed, and the white crystalline precipitate collected, washed with ligroin, and dried in vacuum. We obtained 19.9 g of diphenylzinc (83.3%, calculated on the zinc chloride taken) with m. p. 105° (m. p. according to literature data [5]: 105-107°).

Found %: Zn 29.45; 29.77 $C_{12}H_{10}Zn$. Calculated %: Zn 29.80

Diphenylzinc was soluble in benzene, other aromatic hydrocarbons, carbon tetrachloride, ether, and dioxane, and insoluble in hexane.

Diphenylzinc dioxanate $(C_6H_5)_2Zn \cdot C_4H_8O_2$. 2.8 g of diphenylzinc, obtained as described above, was dissolved in 25 ml of dry dioxane, the bulk of the solvent evaporated and the precipitate collected and washed with ligroin. We obtained 2.5 g of a crystalline substance.

Found %: Zn 20.84; 21.55 $C_{16}H_{18}O_2Zn$. Calculated %: Zn 21.26

Diphenylzinc dioxanate was a crystalline substance, which was readily soluble in dioxane and ether and insoluble in hexane, even on heating. It was readily decomposed by water and alcohol.

Di-o-tolylzinc from crystalline o-tolyllithium. The product was obtained by the procedure described above from 16.5 g (2 moles) of solid o-tolyllithium and 11 g (0.96 mole) of zinc chloride in 100 ml of xylene (with the subsequent addition of 15 ml of absolute ether). Heating for 5 hours and the usual processing yielded 14.1 g of a white crystalline substance with m. p. 69-71° (71% yield, calculated on the zinc chloride taken).

Found %: Zn 26.59; 26.15 $C_{14}H_{14}Zn$. Calculated %: Zn 26.46

Di-o-tolylzinc was a white, crystalline substance, which was soluble in aromatic hydrocarbons, ether, dioxane, and carbon tetrachloride and insoluble in hexane and ligroin.

Di-p-tolylzinc from crystalline p-tolyllithium. By the procedure described above, from 27.7 g (2 moles) of p-tolyllithium and 18.4 g (0.95 mole) of zinc chloride in 100 ml of toluene (with the subsequent addition of 20 ml of absolute ether) we obtained 15 g of di-p-tolylzinc with m. p. 169-170° (45% yield, calculated on zinc chloride).

Found %: Zn 26.28; 26.18 $C_{14}H_{14}Zn$. Calculated %: Zn 26.46

* It is interesting to note that di-α-naphthylzinc could not be prepared directly from di-α-naphthylmercury and zinc [3].

Di-p-tolylzinc was a white, crystalline substance, which was soluble in benzene, dioxane, ether, carbon tetrachloride, and hot xylene and insoluble in hexane, ligroin, and chloroform.

Di-p-tolyzinc dioxanate, $(CH_3C_6H_4)_2Zn \cdot C_4H_8O_2$. 5 g of di-p-tolylzinc was dissolved in 25 ml of dioxane and it yielded 4.8 g of a white, crystalline substance after treatment as described above.

Found %: Zn 19.38; 19.64. $C_{18}H_{22}O_2Zn$. Calculated %: Zn 19.51

It properties were similar to those of diphenylzinc dioxanate.

Di-α-naphthlzinc from crystalline α-naphthyllithium. To a mixture of 21.8 g (0.98 mole) of zinc chloride in 100 ml of toluene was added 20 ml of absolute ether. The mixture was boiled for 5 hours. The di-α-naphthylzinc was difficultly soluble in toluene and therefore the precipitate was collected, dried in vacuum, and extracted with benzene. The yield was 11.62 g (49.5% of theoretical, calculated on the zinc chloride taken). When heated in a sealed capillary (under argon), di-α-naphthylzinc decomposed above 200°.

Found %: Zn 21.01; 20.58. $C_{20}H_{14}Zn$. Calculated %: Zn 20.47

Di-α-naphthylzinc dioxanate $(C_{10}H_7)_2Zn \cdot C_4H_8O_2$. 1 g of di-α-naphthylzinc was dissolved in 15 ml of dioxane. After removal of part of the solvent, the precipitate was collected, washed with ligroin, and dried in vacuum. We obtained 0.88 g of a substance, which was difficultly soluble in ether and dioxane and dissolved in hot benzene.

Found %: Zn 16.09; 16.45 $C_{24}H_{22}O_2Zn$. Calculated %: Zn 16.05

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THE MAGNETIC SUSCEPTIBILITY OF SOME OXALATE COMPLEXES OF TETRAVALENT URANIUM

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The study of the magnetic susceptibility of compounds of tetravalent uranium is of interest in that it provides answers to questions relating to the electronic configuration of tetravalent uranium.

The two unpaired electrons in the tetravalent uranium ion can occupy 6d or 5f orbitals. Then, according to Hund's rules, their ground state will be determined by the terms $^3F_2$ and $^3H_4$, and the effective magnetic moments will be 1.63 and 3.58 Bohr magnetons, respectively, if Russell-Saunders interaction takes place. Since electrons occupying the 6d level are more subject to the effect of the electric fields of the neighboring atoms, the orbital component is generally almost completely quenched, and the magnetic moment in this case is determined only by the spin and is equal to 2.83 μ_B.

The present article reports the results of a study of the magnetic susceptibilities of three oxalate complexes of U(IV):

$$K_4[U(C_2O_4)_4] \cdot 5H_2O,\ Ba_2[U(C_2O_4)_4] \cdot 6H_2O \text{ and } Cd_2[U(C_2O_4)_4] \cdot 7H_2O.$$

The magnetic susceptibilities of these compounds were first studied by A. A. Grinberg and T. K. Fetrazhak [1]. However, the magnetic susceptibilities were determined only at room temperature, and, moreover, corrections were not made for the diamagnetism of the cation and the oxalate ion.

TABLE 1

Analysis of the Oxalate Complexes of Uranium

Compound	Wt. of samples	Uranium		Water		ml $KMnO_4$ consumed, $T = 0{,}00235$ g U/ml
		found,%	calc.,%	found,%	calc.,%	
$K_4[U(C_2O_4)_4] \cdot 5H_2O$	0,1212	28,30		9,83		14,60
	0,0845	28,80	28,45	9,92	10,76	10,00
$Ba_2[U(C_2O_4)_4] \cdot 6H_2O$	0,0775	24,20		11,10	11,11	7,98
	0,1205	23,90	24,48	12,00		12,25
$Cd_2[U(C_2O_4)_4] \cdot 7H_2O$	0,0858	—		14,00		—
	0,1230	24,90	25,10	—	13,40	13,10
	0,0929	—		13,90		—
	0,1080	24,50		—		11,20

We studied the magnetic susceptibilities of these compounds over a broad temperature interval. The values of the Weiss constant and calculation of all diamagnetic corrections made it possible to calculate more accurately the magnetic moments of U(IV) in these salts.

The oxalate complexes of tetravalent uranium were prepared by the method of A. A. Grinberg and T. K. Petrzhak [1]. These compounds were air dried, and were then analyzed for water of crystallization and uranium. The water was determined by drying a weighed sample of the preparation at 105-110° to constant weight. The uranium content was determined by titration of a weighed sample of the complex with potassium permanganate in an atmosphere of CO_2. The analytical results are presented in Table 1.

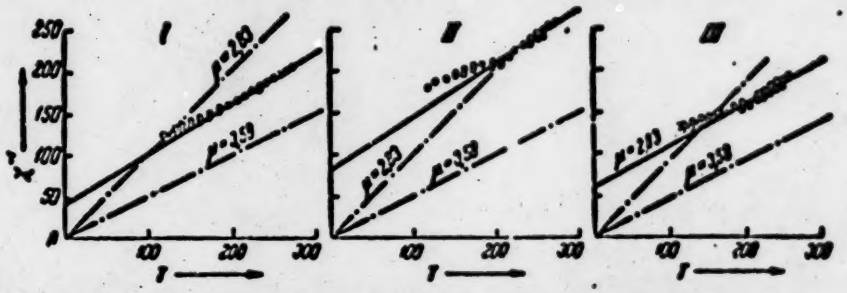

Fig. 1. Relationship between χ^{-1} and absolute temperature for $K_4[U(C_2O_4)_4] \cdot 5H_2O$ (I), $Ba_2[U(C_2O_4)_4] \cdot 6H_2O$ (II), and $Cd_2[U(C_2O_4)_4] \cdot 7H_2O$ (III), and also for μ equals 2.83 and 3.58 μ_B.

The magnetic susceptibility was measured by the Gouy method. The apparatus was fitted with a special accessory which permitted operation over a broad temperature range from room temperature down to liquid nitrogen temperature. Mohr's salt was used as the standard. The effective magnetic moment was calculated by means of the formula $\mu_{eff} = 2.839 \sqrt{\chi^{U^{4+}} (T + \Delta)}$, the magnetic susceptibility was determined from the experimental value of the molar susceptibility $\chi^{U^{4+}}$ after the introduction of appropriate corrections for diamagnetism.

TABLE 2

μ_{eff} and Weiss Constants for Oxalate Complexes of Tetravalent Uranium

Compound	μ_{eff}		Weiss constant, °K	
$K_4[U(C_2O_4)_4] \cdot 5H_2O$				
Sample I	3.62	3.62	58	60±2
Sample II	3.62		62	
$Ba_2[U(C_2O_4)_4] \cdot 6H_2O$				
Sample I	3.57	3.60±0.03	128	132±4
Sample II	3.63		136	
$Cd_2[U(C_2O_4)_4] \cdot 7H_2O$				
Sample I	3.84	3.85±0.01	108	117±9
Sample II	3.86		126	

The Weiss constant was evaluated by means of the equation

$$\Delta = \frac{\chi^{-1}}{\sigma} - 250,$$

where σ is the slope of the linear part of the curve and χ^{-1} is the reciprocal of the susceptibility at 250° K.

The results of the measurements of the magnetic susceptibilities of oxalate complexes of (U(IV) are presented in Table 2 and Fig. 1.

From a consideration of the relationship between magnetic susceptibility and temperature (Fig. 1), it is seen that all of the compounds studied obey the Curie-Weiss law at temperatures above 195° K. There is appreciable deviation from this law at lower temperatures, and the deviation is the same for the different compounds. Similar deviations from the Curie-Weiss law have previously been observed for other compounds [3, 4].

The deviation from the Curie-Weiss law at a temperature below 195° K was apparently due to the emergence of low-temperature magnetic anomalies, and with a decrease in the temperature, the susceptibility begins to increase more slowly than would be expected from the equations

$$\chi = \frac{C}{T + \Delta}.$$

As may be seen from Table 2, the effective magnetic moments of the U (IV) complexes lie within the range of 3.60 to 3.85 Bohr magnetons, which is in good agreement with the theoretical value $\mu_{eff} = 3.58\ \mu_B$. It was pointed out above than an effective magnetic moment of 3.58 μ_B assumes the existence of a spectroscopic state of uranium determined by the term $^3H_4$, and this, in turn, indicates that the two unpaired electrons of tetravalent uranium occupy the 5f level.

In conclusion, the authors express their deep appreciation to V. B. Evdokimov for valuable advice.

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ON THE ACTION OF BROMINE ON 2-ACETOTHIENONE IN THE PRESENCE OF EXCESS ALUMINUM CHLORIDE

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In 1956, Pearson and Pope [1] reported that when acetophenone is brominated in the presence of 2.5-3 moles of anhydrous $AlCl_3$ in a solventless system, the bromine does not enter the side chain, as it usually does in the bromination of this ketone; rather, it enters the nucleus in the meta position to the carbonyl group. In 1958, these same authors established that this method can apparently be used for halogenation of the nucleus of other aromatic carbonyl compounds [2].

The role of the $AlCl_3$ in this reaction probably reduces to a blocking of the acyl group through the formation of a stable hybrid dimeric complex having a cyclic structure.

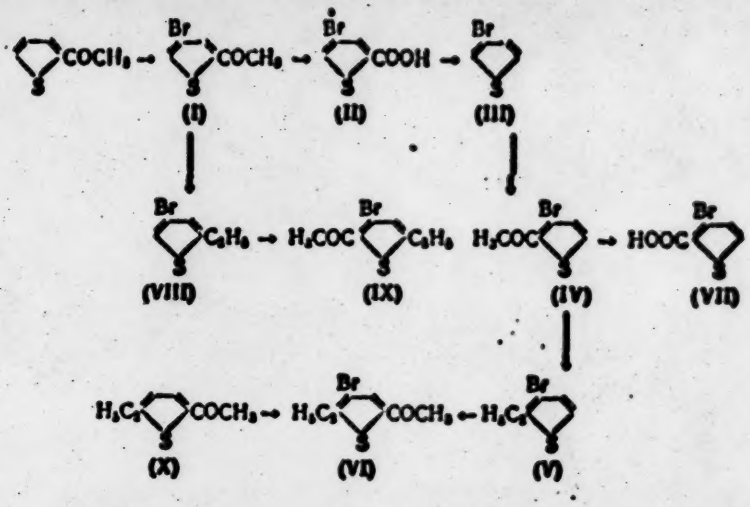
It appeared to be of interest, both from a purely practical and from a theoretical point of view, to study the effect of this unusual method of blocking a side chain on the bromination of alkyl 2-thienyl ketones, for example, 2-acetothienone, which is halogenated exclusively in the side chain under ordinary conditions [3, 4]. In this case, it would be expected that the method used by Pearson and Pope would direct the process toward replacement of a ring hydrogen atom, but, considering the strong α-orienting effect of the sulfur atom, it would be difficult to predict the position (4 or 5) at which substitution would occur.

The literature on electrophilic substitution in thiophene derivatives having a substituent of the second type in the 2-position indicates that the α-orienting effect of the sulfur atom predominates over the directive effect of the meta orienting substituent [5]. Therefore, both nitration and bromination of 2-thiophenecarboxaldehyde [6-9] usually leads to a mixture of the 4- and 5-isomers with a predominance of the 5-isomer.

When we brominated 2-acetothienone in the presence of 2.5 moles of anhydrous $AlCl_3$ in a solventless system, 4-bromo-2-acetothienone (I), previously undescribed in the literature, was obtained. 4,5-Dibromo-2-acetothienone was obtained as a by-product; the structure of this compound was confirmed by oxidation to the known 4,5-dibromo-2-thiophenecarboxylic acid [10]; 5-bromo-2-acetothienone was not found in the reaction products.

The structure of bromo-substituted ketone I was proved by two routes (see scheme). Oxidation gave the known 4-bromo-2-thiophenecarboxylic acid (II), and decarboxylation of the latter gave 3-bromothiophene (III); acetylation of the latter gave 3-bromo-2-acetothienone (IV), which was described, though without proof of structure, by Steinkopf and co-workers [10]. Reduction of the 3-bromo-2-acetothienone by Kishner reduction gave the previously undescribed 3-bromo-2-ethylthiophene (V), and acetylation of the latter gave 4-bromo-5-ethyl-2-acetothienone (VI). Similarly, oxidation of the 3-bromo-2-acetothienone (IV) to the known 3-bromo-2-thiophenecarboxylic acid (VII) [10] confirmed the structure of this ketone.

The second route comprised Kishner reduction of 4-bromo-2-acetothienone (I) to 4-bromo-2-ethylthiophene, and acetylation of this compound to 3-bromo-5-ethyl-2-acetothienone (VIII). Similarly, bromination of 5-ethyl-2-acetothienone (X) by the method of Pearson and Pope [2] gave the ketone (VI), the semicarbazone of which proved to be identical to the semicarbazone of the product obtained by acetylation of 3-bromo-2-ethylthiophene (V). Compounds VI, VIII, and IX also have not been described in the literature.



That the melting points of the semicarbazones of VII and IX were different constitutes additional proof that the bromination of 2-acetothienone proceeds in the 4 position of the thiophene ring.

Use of the bromination method described here and the high yields of the products formed in the majority of the stages open up new possibilities for the synthesis of relatively unavailable thiophenes. Thus, the method of Pearson and Pope has been successfully used in our laboratory for the introduction of a second acetyl group into 2-acetothienone and for the chloromethylation of it. Detailed data on this problem will be published later.

EXPERIMENTAL

Bromination of 2-acetothienone. Over a period of 10 minutes, 25 g of 2-acetothienone was added dropwise, with stirring, to 66.3 g of anhydrous $AlCl_3$. 12.5 ml of dry bromine was added dropwise over a period of 10 minutes to the liquid complex at 30-40°. The congealed mass was transferred to a mixture of ice and 68 ml of concentrated HCl. The oil which separated was extracted with ether, and the extract was washed with water and with a solution of soda, dried over $CaCl_2$, and distilled under vacuum. The following fractions were collected: I) b. p. 133-143°/15 mm, 28.6 g, n_D^{20} 1.6110; II) B. P. 143-170°/15 mm, 7.8 g, m. p. 77-80°.

A second distillation of Fraction I gave 26.8 g of 4-bromo-2-acetothienone (I) with a b. p. of 133-135°/15 mm, 125-127°/11 mm, 117-119°/7 mm, n_D^{20} 1.6080, yield 66% of theoretical.

C_6H_5BrOS.	Found %:	C 34,95; 35,07;	H 2,46; 2,28
	Calculated %:	C 35,19;	H 2,46

M. p. of semicarbazone, 214.5-215° (from alcohol).

$C_7H_8BrN_3OS$.	Found %:	N 15,58;	15,49
	Calculated %:	N 16,09	

M. p. of phenylhydrazone, 109.5-110° (from alcohol).

$C_{12}H_{11}BrN_2S$.	Found %:	C 48,44;	48,50;	H 3,87;	3,90;	N 9,70;	9,63
	Calculated %:	C 48,83;		H 3,76;		N 9,49	

Fraction II (yield 13.5%) was 4,5-dibromo-2-acetothienone, which, after recrystallization from aqueous alcohol, melted at 85-86° (literature value [10]: 85-86°).

$C_6H_4Br_2OS$.	Found %:	C 25,40;	25,34;	H 1,42;	2,37
	Calculated %:	C 25,41;		H 1,42	

4-Bromo-2-thiophenecarboxylic acid (II). The oxidation of 4-bromo-2-acetothienone was carried out by the method described in the literature for the oxidation of 2-acetothienone [10]. Oxidation of 14.7 g of the ketone in a mixture of 9.6 g of NaOH, 34.7 g of $KMnO_4$, and 7.5 ml of 30% H_2O_2 gave 12.3 g of 4-bromo-2-thiophenecarboxylic acid; 82.5% yield, m. p. 121-122° (from water) (literature value [7]: 122-123.5°).

	Found %	: C 29,28; 29,30;	H 1,44; 1,38
$C_5H_3BrO_2S$.	Calculated %:	C 29,00;	H 1,48

4,5-Dibromo-2-thiophenecarboxylic acid was prepared under conditions similar to those used in the preparation of II; 2.7 g of 4,5-dibromo-2-acetothienone, 1.3 g of NaOH, 4.6 g of $KMnO_4$, and 0.9 ml of 30% H_2O_2 were used. The acid was recrystallized from benzene; 27.4% yield, m. p. 227-228° (literature value [10], 227-228°).

	Found %.	: C 21,39; 21,17;	H 0,77; 0,58
$C_5H_2Br_2O_2S$.	Calculated %:	C 21,17;	H 0,70

3-Bromothiophene (III). The decarboxylation of 17.2 g of 4-bromo-2-thiophenecarboxylic acid were carried out in 80 ml of distilled quinoline in the presence of ~10 mg of copper powder at a bath temperature of 220-240°. 1750 ml of CO_2 (theoretical, 1860 ml) was evolved in 1.25 hours. The reaction mixture was poured into 400 ml of water, acidified with HCl to an acid reaction toward congo indicator, and extracted with ether. The extract was washed with water and with a solution of soda. The 3-bromothiophene was distilled from a flask fitted with a dephlegmator. 11.8 g of product with a b. p. of 158-160°, n_D^{20} 1.5860, was collected; the yield was 87.2%. Literature data [10]: b. p. 157-158°, $n_D^{19.8}$ 1.5861.

3-Bromo-2-acetothienone (IV). To a solution of 11 g of 3-bromo-thiophene and 6.3 g of distilled CH_3COCl in 21 ml of dry benzene, cooled to ~0°, was added dropwise over a period of 30 minutes a solution of 10.8 g of anhydrous stannic chloride in 7 ml of dry benzene. On the following day, 35 ml of 6 % HCl was added dropwise at 5-10°. The benzene layer was washed with water and a solution of soda. The aqueous layer and the wash water were extracted with benzene, and the material remaining after distillation of the benzene and the combined benzene solutions were distilled. 7.1 g of 3-bromo-2-acetothienone, n_D^{20} 1.6108, was collected; 51.8% yield, b. p. 102-105°/4 mm. Literature value [10], 130°/11 mm.

	Found %:	C 35,47; 35,70;	H 2,41; 2,58
C_6H_5BrHS	Calculated %:	C 35,19;	H 2,45

M. p. of semicarbazone 196.5-198° (from alcohol).

	Found %:	N 15,84; 15,57	
$C_7H_8BrN_3OS$.	Calculated %:	N 16,08	

3-Bromo-2-thiophenecarboxylic acid (VII) was prepared by oxidation of 1 g of 3-bromo-2-acetothienone with 2.4 g of $KMnO_4$ and 0.5 ml of 30% H_2O_2 in the presence of 0.7 g of NaOH. The yield of acid was 49%, m. p. 197-197.5° (from water). Literature value [10], 190°.

	Found %:	C 29,01; 28,78;	H 1,55; 1,38
$C_5H_3BrO_2S$	Calculated %:	T 29,00;	H 1,48

3-Bromo-2-ethylthiophene (V). A mixture of 7 g of 3-bromo-2-acetothienone, 8.4 g of hydrazine hydrate, and 21 g of ethylene glycol was heated until the mixture became completely homogeneous (at 30°). 8.4 g of granulated KOH was introduced at 40°. The mixture was heated over a burner until the distilled material was transparent. The distillate was extracted with ether. The extract was washed with 10% HCl, a solution of soda, and water, and dried over $CaCl_2$. The ether was distilled, and the residue was distilled under vacuum. 4.5 g of 3-bromo-2-ethylthiophene was collected; b. p. 79-81°/14 mm, n_D^{20} 1.5602, 69% yield.

C_6H_7BrS.	Found %:	C 38,30;	38,21;	H 3,82;	3,87
	Calculated %:	C 37,70;		H 3,69	

4-Bromo-5-ethyl-2-acetothienone (VI). The acetylation was carried out under conditions similar to those used for the preparation of 3-bromo-2-acetothienone; the initial temperature during the addition of the $SnCl_4$ was −10°. From 3.9 g of 3-bromo-2-ethylthiophene, 1.8 g of CH_2COCl, and 3.1 g of $SnCl_4$ was obtained 2.8 g of VI, b. p. 124-126°/4 mm, n_D^{20} 1.5800, 55.8% yield. The product distilled with mild decomposition.

M. p. of semicarbazone, 235-236° (from alcohol; in a sealed capillary).

$C_9H_{12}BrN_3OS$.	Found %:	C 37,20;	37,05;	H 4,02;	4,00
	Calculated %:	C 37,25;		H 4,17	

Bromination of 5-ethyl-2-acetothienone. To 21.8 g of $AlCl_3$ was added dropwise 10 g of 5-ethyl-2-acetothienone and, at 30-40°, 3.8 ml of dry bromine. After 2.5 hours, the mixture solidified. It was transferred to a mixture of ice and 25 ml of concentrated HCl, and was then treated as described above. The following fractions were collected during distillation: I) b. p. 121-131°/4 mm, 7.9 g, n_D^{20} 1.5918; II) b. p. 131-153°/4 mm, 3.7 g, n_D^{20} 1.6093.

The substance distilled with partial decomposition. Redistillation of Fraction I gave 4.5 g of VI, b. p. 119-121°/4 mm, n_D^{20} 1.5882; 36.8% yield. Fraction II was not investigated.

A mixture of the semicarbazone, m. p. 235-236°, with the semicarbazone obtained from VI synthesized by the other route melted without depression of the melting point.

4-Bromo-2-ethylthiophene (VIII) was prepared by Kishner reduction (see above) of 17.6 g of 4-bromo-2-acetothienone with 21 g of hydrazine hydrate, 51 g of ethylene glycol, and 21 g of KOH. The mixture was heated to 100° for the formation of the hydrazone. 13.6 g of 4-bromo-2-ethylthiophene was obtained, b. p. 81.5-82.5°/14 mm, n_D^{20} 1.5617, 83% yield.

C_6H_7BrS.	Found %:	C 37,99;	37,78;	H 3,93;	3,87
	Calculated %:	C 37,72;		H 3,69	

3-Bromo-5-ethyl-2-acetothienone (IX) was prepared under conditions similar to those used for the preparation of VI from 8.3 g of 4-bromo-2-ethylthiophene, 3.7 g of CH_2COCl, and 6.7 g of $SnCl_4$. Redistillation under vacuum gave 6.1 g of IX, b. p. 122-125°/3 mm, n_D^{20} 1.5833, 61% yield.

C_8H_9BrOS.	Found %:	C 41,36;	41,37;	H 3,90;	3,82
	Calculated %:	C 41,28;		H 3,89	

M. p. of semicarbazone, 188-191° (from alcohol; in a sealed capillary).

$C_9H_{12}BrN_3OS$.	Found %:	C 37,31;	37,30;	H 4,08;	4,05
	Calculated %:	C 37,25;		H 4,17	

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THE CONDENSATION OF HALO ALCOHOLS WITH BENZENE UNDER THE INFLUENCE OF SULFURIC ACID

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In our preceding investigation [1], we studied the haloalkylation of benzene with methallyl chloride and 2-methylpropenyl bromide in the presence of 100% H_2SO_4. The yield of chloro-tert-butylbenzene was 74%, while that of bromo-tert-butylbenzene was 35%. More recently, we have been sucessful in obtaining these same products in yields of 70 and 25%, respectively, by the condensation of 2-methylpropenyl chloride and methallyl bromide with benzene. An attempt to extend the haloalkylation reaction to dichloroolefins – 1,1-dichloro-2-methyl-2-propene, 1,3-dichloropropene, and 1,2-dichloro-2-propene – was unsuccessful. Schmerling and co-workers [2] were also unsuccessful in attempts to carry out the condensation of these dichloroolefins with benzene in the presence of sulfuric acid.

A number of examples of the haloalkylation of benzene with tertiary halo alcohols were studied in the present investigation. The change from haloalkenes to halo alcohols was dictated partly by the circumstance that this permits the synthesis of a larger number of chloro-and bromoalkylbenzenes of different structures. The structures of the halo alcohols, the conditions under which the condensation reactions were carried our, the ratios of reagents, and the product yields are presented in Table 1; the properties of the condensation products are presented in Table 2. It was previously established that in the condensation of 1-chloro-2-propanol with benzene in the presence of BF_3, 1-chloro-2-phenylpropane is formed in 37% yield [3]. We were unable to carry out this reaction by contacting the reactants with 90% H_2SO_4 for six hours. A large part of the 1-chloro-2-propanol was recovered from the reaction mixture. As Kundiger and Pledger have shown [4], the alkylation of benzene with a tertiary alcohol – 1,1,1-trichloro-2-methyl-2-propanol – in the presence of $AlCl_3$ yields 3,3-dichloro-2-methylallylbenzene; i.e., the reaction proceeds at the expense of a chlorine atom of the 1,1,3-trichloro-2-methyl-1-propene formed as an intermediate.

Of the homologous tertiary monochloro alcohols $ClCH_2C(CH_3)_2OH$, $ClCH_2CH_2C(CH_3)_2OH$, and $ClCH_2CH_2CH_2C(CH_3)_2OH$, we were able to obtain chloroalkylation products only with the first and third. The method used for the condensation of the halo alcohol with benzene was the same in all cases. The calculated amount of H_2SO_4 was added, with stirring, to the reagents over a period of 1.5-2 hours, after which the reaction mixture was stirred for an additional several hours (Table 1). In the reaction of 1-chloro-2-methyl-2-propanol with benzene, that part of the alcohol which did not enter into the condensation reaction was recovered from the reaction mixture. 1-bromo-2-methyl-2-propanol behaved similarly. With a change in the order of addition of the reactants, i.e., when the 1-chloro-2-methyl-2-propanol was added to a mixture of benzene and 80% H_2SO_4, no alkylation product was obtained. The second member of the series, 1-chloro-3-methyl-3-propanol, was evidently partially dehydrated under the conditions of the reactions (60% was dehydrated; about 40% of the alcohol was recovered from the reaction mixture); however, the resulting 1-chloro-3-methyl-2-butene did not alkylate the benzene, but instead rearranged to 2-chloro-2-methyl-3-butene. HCl was eliminated from the latter with the formation of isoprene, which polymerized under the influence of the H_2SO_4 (only a wide-boiling fraction of hydrocarbons was separated from the reaction products). Under the conditions employed, more than half of the 1-chloro-4-methyl-4-pentanol cyclized to 2,2-dimethyltetrahydrofuran, which explains the low yield of condensation product. The presence of a quaternary carbon atom in the latter was confirmed by the infrared spectrum. The alkylation of

benzene with 1,1-dichloro-2-methyl-2-propanol gave a 15% yield of 1,1-dichloro-2-methyl-2-phenylpropane. The major part of the original alcohol (74.5%) was dehydrated with the formation of dichloroisobutylenes, $CH_2 = C(CH_3)CHCl_2$ and $ClCH = C(CH_3 - CH_2Cl$, which, as we have noted, are incapable of condensing with benzene.

TABLE 1

	Alcohol	Mole ratio C_6H_6 : alcohol : H_2SO_4	H_2SO_4 conc., %	Reaction temp., °C	Stirring time, hr.	Haloalkylation product	Yield, %
I	$ClCH_2C(CH_3)_2OH$	3 : 1 : 10	80	3–5	7	$ClCH_2C(CH_3)_2C_6H_5$	17
	$ClCH_2C(CH_3)_2OH$	3 : 1 : 10	90	3–5	5	$ClCH_2C(CH_3)_2C_6H_5$	50,6
	$ClCH_2C(CH_3)_2OH$	3 : 1 : 10	95	3–5	7	$ClCH_2C(CH_3)_2C_6H_5$	50,5
II	$ClCH_2CH(CH_3)OH$	3 : 1 : 10	90	3–5	6		
III	$BrCH_2C(CH_3)_2OH$	3 : 1 : 10	90	7	7	$BrCH_2C(CH_3)_2C_6H_5$	35,8
IV	$Cl_3CHC(CH_3)_2OH$	3 : 1 : 10	90	3–5	8	$Cl_3CHC(CH_3)_2C_6H_5$	15
	$Cl_3CHC(CH_3)_2OH$	3 : 1 : 10	90	3–5	5,5	$Cl_3CHC(CH_3)_2C_6H_5$	7,5
V	$ClCH_2C(C_2H_5)_2OH$	3 : 1 : 10	90	3–6	4	$ClCH_2C(C_2H_5)_2C_6H_5$	29,8
VI	$ClCH_2CH_2C(CH_3)_2OH$	3 : 1 : 10	90	3–6	6		
VII	$ClCH_2CH(CH_3)C(CH_3)_2OH$	3 : 1 : 10	90	3–6	9		
VIII	$ClCH_2CH_2CH_2C(CH_3)_2OH$	3 : 1 : 10	80	3–5	4	$ClCH_2CH_2CH_2C(CH_3)_2C_6H_5$	23
	$ClCH_2CH_2CH_2C(CH_3)_2OH$	3 : 1 : 10	80	5–10	9	$ClCH_2CH_2CH_2C(CH_3)_2C_6H_5$	23
	$ClCH_2CH_2CH_2C(CH_3)_2OH$	3 : 1 : 10	90	3–5	8,5	$ClCH_2CH_2CH_2C(CH_3)_2C_6H_5$	35

1-Chloro-2-ethyl-2-buranol also partially dehydrated under the influence of H_2SO_4. An attempt to chloroalkylate benzene with the chlorooleflin formed by the dehydration of this alcohol was unsuccessful.

We found that the best yields are obtained when 90% H_2SO_4 is used; an increase or decrease in its concentration decreases the yield.

EXPERIMENTAL

Halo alcohols. The 1-chloro-2-methyl-2-propanol and 1-chloro-2-propanol were prepared by sulfuric acid hydration of methallyl chloride and allyl chloride [5]. 1-Chloro-3-methyl-3-butanol was obtained in 72% yield by Grignard reaction from CH_3MgCl and β-chloro-methylpropionate [an ester of 3-chloropropionic acid]; b. p. 82-84°/29 mm, d_4^{20} 1.0308; n_D^{23} 1.4455; MR_D found 31.68; MR_D calc. 31.65.

$C_5H_{11}OCl$ Found %: C 48,58; 48,54; H 8,93; 8,97
Calculated %: C 48,98; H 9,05

1-Bromo-2-methyl-2-propanol was similarly obtained in 41% yield from methyl bromoacetate; b. p. 62-65°/3 mm, d_4^{20} 1.3402; n_D^{20} 1.4513; MR_D found 30.77; calc. 29.89.

1,1-Dichloro-2-methyl-2-propanol was similary obtained in 35% yield from methyl dichloracetate; b. p. 53-56°/21 mm, d_4^{20} 1.2473; n_D^{20} 1.4630; MR_D found 31.58; MR_D calc. 31.84.

1-Chloro-2-ethyl-2-butanol was similarly obtained in 82% yield from methyl chloroacetate; b. p. 93-94°/60 mm; d_4^{20} 1.0117; n_D^{20} 1.4502; MR_D found 36.02; MR_D calc. 36.36.

1-Chloro-4-methyl-4-pentanol was prepared in 65% yield from γ-chloropropyl methyl ketone and CH_3MgCl; b. p. 67-68°/2 mm, d_4^{20} 1.0154; n_D^{20} 1.4495; MR_D found 36.13; MR_D calc. 36.30.

The γ-chloropropyl methyl ketone was prepared by the action of concentrated hydrochloric acid on acetopropyl alcohol [γ-hydroxypropyl methyl ketone] [6].

The 1-chloro-2,3-dimethyl-3-butanol was prepared in two steps. Hydrogen chloride, dried with concentrated H_2SO_4 and P_2O_5, was bubbled through 13.15 g of methyl methacrylate at room temperature, and the mixture was stirred for 7 hours. From the reaction mixture was obtained untreated methyl methacrylate and 165 g of

γ-chloromethyl isobutyrate with a b. p. of 154-155°, d_4^{20} 1.1133; n_D^{20} 1.4278; MR_D found 31.54; MR_D calc. 31.88. Treatment of this chloro ester with methylmagnesium chloride gave 1-chloro-2,3-dimethyl-3-butanol in 72% yield; b. p. 81-82°/21 mm, d_4^{20} 1.0272; n_D^{20} 1.4540; MR_D found 36.05; MR_D calc. 36.30.

Condensation of chloro alcohols with benzene. The condensation reactions were carried out in a round-bottom flask fitted with a stirrer, a dropping funnel, and a thermometer. The chloro alcohols were used in amounts of 30-70 g. A description of a typical synthesis follows. 240 g (2.2 moles) of 90% H_2SO_4 was added, with vigorous stirring and over a period of 1.5 hours, to a mixture of 50.7 g (0.65 mole) of benzene and 30 g (0.22 mole) of

TABLE 2

Haloalkylation product	B. p., °C/mm	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Calc., % C	Calc., % H
$C_6H_5C(CH_3)_2CH_2Cl$ *	112—113°/23	1,0359	1,5235	49,07	49,64	—	—	—	—
$C_6H_5C(CH_3)_2CH_2Br$ **	77—78°/2	1,2783	1,5438	52,61	52,76	—	—	—	—
$C_6H_5C(CH_3)_2CHCl_2$	88,5—91°/1,5	1,1686	1,5300	54,45	54,61	58,79 58,08	5,70 5,83	59,13	5,98
$C_6H_5C(C_6H_5)_2CH_2Cl$	98—100°/3	1,0117	1,5168	59,18	59,18	73,24 73,10	8,79 8,85	73,26	8,68
$C_6H_5C(CH_3)_2CH_2CH_2CH_2Cl$	128—129°/15	1,0107	1,5158	58,70	59,18	72,48 72,61	8,72 8,56	73,26	8,68

*Lit. data [9]: b. p. 95°/10 mm; d_4^{25} 1.0379; n_D^{20} 1.5249.

**B. p. 97°/6 mm; d_4^{25} 1.2789; n_D^{20} 1.5470.

1-chloro-4-methyl-4-pentanol at a temperature of 3-5°. The addition of the first portions of acid caused a rise in the temperature of the reaction mixture to 9°. After the addition of the chloro alcohol was complete, the reaction mixture was stirred for another 7 hours; it was then poured onto ice, and the organic layer was separated from the aqueous layer, washed, and dried over $CuSO_4$. Vacuum distillation of the organic layer gave 11.2 g (51% yield) of 1,1-dimethyltetrahydrofuran with a b. p. of 91-97°, d_4^{20} 0.8408; n_D^{20} 1.4084. Literature data [7]: b. p. 92°, d_4^{20} 0.8422; n_D^{20} 1.4068 and 15 g (35% yield) of 1-chloro-4-methyl-4-phenylpentane was also obtained. The instability of 1-chloro-4-methyl-4-pentanol and the formation from it on heating of 2,2-dimethyltetrahydrofuran has already been noted [8].

2-Methyl-2-phenylpentane. The organomagnesium compound of 1-chloro-4-methyl-4-phenylpentane was prepared; this was decomposed to form 2-methyl-2-phenylpentane with a b. p. of 61.5°/2.5 mm, d_4^{20} 0.8679; n_D^{20} 1.4910. Analysis of the infrared spectrum showed that this hydrocarbon had a quaternary carbon atom in the alkyl radical.

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ON SOME ESTERS OF ETHYLVINYL- AND ETHYLALLYLPHOSPHINIC ACIDS

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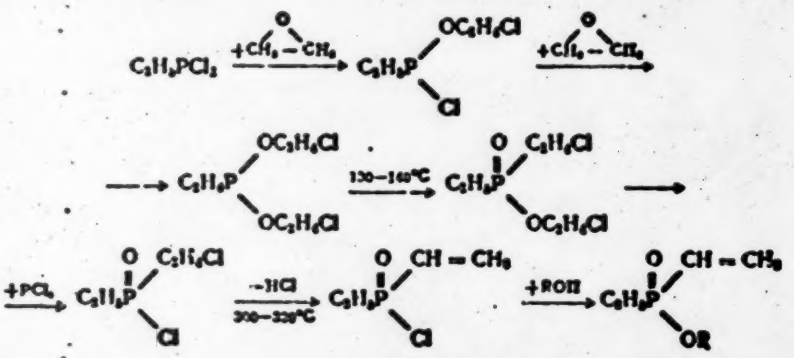
(Presented by Academician A. E. Arbuzov, May 28, 1959)

Investigations of the polymerization of allyl esters of arylphosphonic acids [1] and also of certain esters of vinylphosphonic acid [2] have instigated an increased interest in unsaturated organic compounds of phosphorus. Beginning in 1948, one of the authors and his co-workers have carried out a series of investigations concerned with the synthesis, polymerization, and copolymerization of certain unsaturated organophosphorus compounds [3-5]. The present work is a continuation of the investigations in our laboratory in the field of the synthesis and polymerization of unsaturated esters of phosphorus acids.

The synthesis of esters of ethylvinylphosphinic acid was carried out in several steps. The reactions may be schematically represented as follows



The interaction of ethyldichlorophosphine [6] with ethylene oxide proceeds smoothly in a medium of absolute ethyl ether with the formation of the acid chloride of β-chloroethoxyethylphosphonous acid [β-chloroethylethylchlorophosphine] and, depending on the number of molecules of ethylene oxide entering into the reaction, di-β-chloroethyl ethylphosphonite. The latter is a colorless liquid with a weak odor of phosphine. The ester is stable during distillation; however, it slowly oxidizes in air, reacts vigorously with sulfur, and interacts with cuprous chloride with the evolution of a great amount of heat. The latter fact indicates that the phosphorus is trivalent.

Studying the properties of tris-β-chloroethyl phosphite, M. I. Kabachnik and P. A. Rossiiskaya [7] established that in the presence of halogen the atoms brought about an internal rearrangement of the ester at elevated temperatures with conversion of the phosphorus from the trivalent to the pentavalent state. Considering that esters of alkylphosphonous acids are considerably more reactive than complete phosphites [8], in our case it would be expected that isomerization of di-β-chloroethyl ethylphosphonite to the corresponding ester of ethyl-β-chloroethylphosphinic acid would proceed considerably more easily. Indeed, after the ester had been heated in boiling ethylbenzene (in an atmosphere of nitrogen and with vigorous stirring) for 1 hour, vacuum distillation failed to

TABLE 1

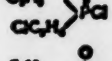
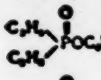
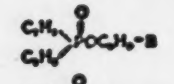
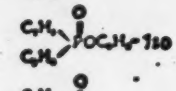
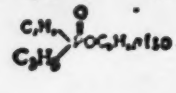
Formula	B. p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	% P found	% P calc	% Cl found	% Cl calc	Yield, %
Esters of ethylvinylphosphinic acid										
	46/8	1,4860	1,2200	41,20	41,18	18,00	17,70	40,30	40,58	
	92/5	1,4795	1,2030	51,70	51,77	14,16	14,10	32,50	32,36	75
	132—134/4	1,4832	1,2600	49,33	49,38	14,32	14,10	32,00	32,36	60
	127/10	1,4900	1,2985	38,94	38,88	17,84	17,70	40,71	40,58	50
	86—88/3	1,4584	1,1300	44,60	44,52	17,00	16,75	19,30	19,20	30
	90/10	1,4805	1,1695	33,65	33,54	22,28	22,40	25,83	25,60	60
	107/7	1,4695	1,1610	43,85	44,05	17,11	16,98	19,70	19,42	30
	80/11	1,4518	1,0500	34,43	34,57	23,18	23,11	—	—	70
	86,5/14	1,4495	1,0210	38,90	39,18	20,93	20,91	—	—	50
	94—95/10	1,4468	0,9851	43,96	43,80	19,23	19,06	—	—	62
	83/10	1,4440	0,9777	44,07	43,80	19,18	19,06	—	—	30
	99—100/10	1,4640	1,0160	43,46	43,34	19,26	19,30	—	—	60
	106/10	1,4472	0,9716	48,48	48,42	17,44	17,54	—	—	80
	99—100/10	1,4448	0,9674	48,45	48,42	17,65	17,54	—	—	80
	112/10	1,4466	0,9561	53,11	53,04	16,45	16,30	—	—	80
Esters of ethylallylphosphinic acid										
	115—117/12	1,4672	1,0100	47,86	47,95	17,74	17,78	—	—	70
	111—112,5/10	1,4480	0,9792	48,35	48,42	17,67	17,60	—	—	50
	98—99/10	1,4450	0,9701	48,31	48,42	17,65	17,60	—	—	20

TABLE 1 (continued)

Formula	B. p., °C/mm Hg	n_D^{20}	d_4^{20}	MRD found	MRD calc.	%P found	%P calc.	%Cl found	%Cl calc.	Yield, %
	120–122/10	1,4495	0,9070	52,80	53,01	16,29	16,29	—	—	35
	110–118/10	1,4470	0,9590	53,00	53,01	16,05	16,29	—	—	40
	120–132/10	1,4485	0,9500	57,55	57,66	14,80	15,17	—	—	45

isolate any of the ester of the trivalent phosphorus acid; the latter had been almost completely isomerized.

The interaction of the β-chloroethyl ester of ethyl-β-chloroethylphosphinic acid with phosphorus pentachloride in an 8-fold amount of ethyl ether gave the chloride of the corresponding acid. When the latter was passed at a temperature of 300-320° through a quartz tube packed with calcined barium carbonate, it readily split out hydrogen chloride with the formation of ethylvinylphosphinyl chloride. This product was a colorless, mobile liquid with a [illegible]reminiscent of phosphoryl chloride, it fumed weakly in air, decomposed in water, and added bromine.

The esters of ethylvinylphosphinic acid were prepared by the interaction of the acid chloride with the appropriate alcohol in the presence of pyridine in a medium of absolute ether. These esters were colorless, mobile liquids, and all of them (with the exception of the β-chloroethyl ester) were miscible with water and had a weak but agreeable fruit-like odor. The constants of these compounds are presented in Table 1.

The esters of ethylallylphosphinic acid were prepared by Arbuzov rearrangement of the corresponding esters of ethylphosphonous acid [8, 9] with allyl bromide.

The reaction was carried out either in a sealed tube with a mole-per-mole component ratio and at a temperature of 60-80° for 4 hours, or directly in a distillation flask by the dropwise addition of the ethylphosphonous acid ester to a 2-3-fold excess of allyl bromide, which was heated to its boiling point.

All the esters of ethylallylphosphinic acid were colorless, mobile liquids with a weak, somewhat sharp odor, and were readily miscible with water at ordinary temperatures (with the exception of the isoamyl ester). The constants of these compounds are presented in Table 1. We carried out preliminary experiments on the polymerization of these esters of ethylvinyl- and ethylallylphosphinic acid. The reaction was carried out in sealed tubes at a temperature of 80-120°. Benzoyl peroxide in an amount of 2% of the ester investigated was added as a polymerization initiator. Briefly, the results were the following.

The esters of ethylvinylphosphinic acid polymerized over the course of 20-40 hours to a colorless or slightly yellow gelatinous mass. Some of the polymer samples (of the n-propyl and isobutyl esters) completely lost the property of flowing. The allyl ester polymerized over a period of 4 hours to a colorless or slightly yellow waxy mass.

Of the esters of ethylallylphosphinic acid, the allyl ester readily polymerized, and, over the course of 8 hours, it formed a yellow, waxy mass. The remaining esters of ethylallylphosphinic acid became yellow on prolonged heating (over a period of 6 days), but their consistency was almost unchanged.

EXPERIMENTAL

Di-β-chloroethyl ester of ethylphosphonous acid (I). 100 ml of absolute ether and 20 g of ethyldichlorophosphine were placed in a three-neck flask fitted with a thermometer, a reflux condenser, and a mechanical stirrer. After the system had been purged with nitrogen, a stream of ethylene oxide was passed through the vigorously stirred mixture, which was externally cooled; the ethylene oxide was introduced at a rate such that the

temperature of the mixture was maintained at from +15 to +30° C. The reaction was considered to be complete when the temperature failed to increase upon removal of the cooling means. The stream of ethylene oxide was then replaced by a stream of nitrogen, and the ether was distilled from the reaction mixture. 27 g of (I) was separated from the mixture by distilling it twice.

β-Chloroethyl ester of ethyl-β-chloroethylphosphinic acid (II). 18 g of (I) in 100 ml of ethylbenzene was heated in a flask fitted with a reflux condenser at a mixture temperature of 138-140°; the reaction mixture was vigorously stirred. A stream of nitrogen was continuously passed into the system. After 1 hour, the refractive index of the mixture had changed from 1.4900 to 1.4920. The mixture was distilled under vacuum. 12 g of the pure ester (II) was obtained.

Ethyl-β-chloroethylphosphinyl chloride (IV). A suspension of 24 g of phosphorus pentachloride in 150 ml of absolute ether was prepared in a three-neck flask. The suspension was vigorously stirred, and 25 g of II was added from a dropping funnel. The temperature of the mixture was maintained at 5-15°. After the addition had been completed, the precipitate disappeared, and the solution became homogeneous. The ether was distilled, and the residue was distilled under vacuum. 11 g of IV was obtained.

Ethylvinylphosphinyl chloride (V). 120 g of IV was introduced dropwise into a quartz tube, which was mounted at a slight angle (20°); the vapors passed through the tube at a temperature of 300-320°, and 30 minutes was required for the passage of the 120 g. 70 g acid chloride V was obtained.

Ethyl ester of ethylvinylphosphinic acid (VI). 12 g of V was added dropwise to a vigorously stirred mixture of 100 ml of absolute ether, 5 g of absolute ethanol, and 7 g of pyridine, which was externally cooled. The temperature of the mixture was maintained at 12-15°. After completion of the addition, the mixture was heated to the boiling point of the ethyl ether; it was maintained at this temperature for 10-15 minutes, and then cooled. The precipitated pyridine hydrochloride was filtered, and the precipitate was washed on the filter several times with small portions of ether. The ethyl ether was distilled from the filtrate, and distillation of the residue under vacuum gave 6 g of VI.

All of the other esters of ethylvinylphosphinic acid were similarly prepared by this method, with the one difference that the temperature of the reaction mixture was maintained within the range of from −6 to +5°. This change increased the yield from 60 to 80%.

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REGULARITIES IN THE ISOMERIZATION OF THE DOUBLE BONDS IN CYCLOHEXADIENE-1,2-DICARBOXYLIC ACIDS

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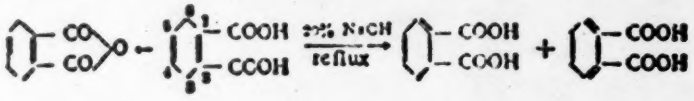
(Presented by Academician B. A. Kazanskii, June 2, 1959)

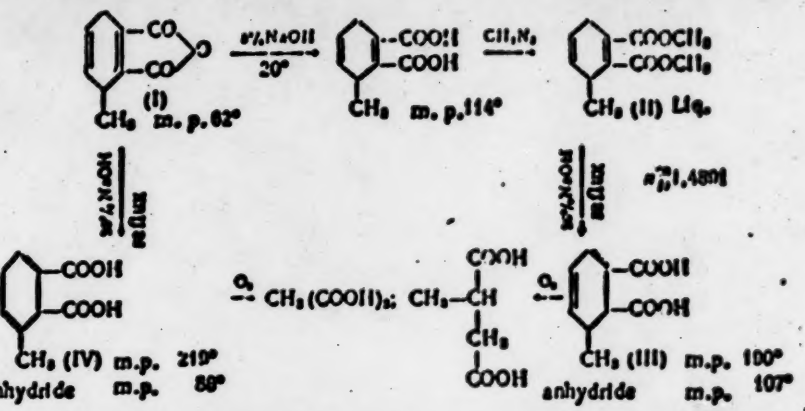
It was shown in one of our preceding communications [1] that the double bond system in cyclohexadiene-1,2-dicarboxylic acids, which may be obtained by thermal or alkaline cleavage of 3-acetoxycyclohexene-1,2-dicarboxylic acids, is capable of undergoing a specific isomerization similar to that noted earlier by Baeyer [2]. He established that the unconjugated $\Delta^{1,6}$ double bond system is stable only when an anhydride ring is present, and that it can isomerize during alkaline saponification with a shift to $\Delta^{4,6}$ and $\Delta^{3,6}$ -systems.



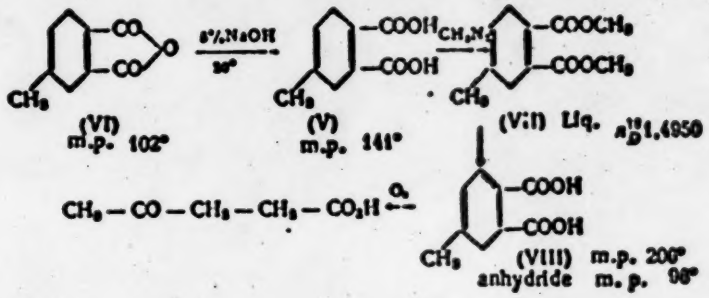
Despite the fact that individual examples of such double bond shifts have also been noted by other authors [3-5], relatively little study has been made of them; such studies as have been made include the adducts of various dienes with acetylene dicarboxylic acid. Only in one of Alder's papers has attention been given to the possibility of isomerization of this type [6].

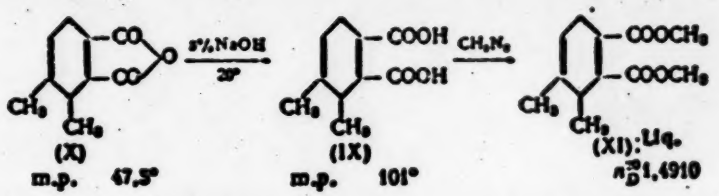
With the aim of systematically tracing the nature and regularities in double bond isomerization in $\Delta^{1,6}$-cyclohexadiene-1,2-dicarboxylic acids, we studied the transformations of homologs of dihydrophthalic acid with methyl groups at various positions in the ring; these compounds were prepared by condensation of various dienes with acetylenedicarboxylic acid and its dimethyl ester. The first compounds to be investigated were the anhydride of 3-methyl-$\Delta^{1,6}$-cyclohexadiene-1,2-dicarboxylic acid (I) and the diester (II), both of which we prepared. It was found that, as in the case of the unsubstituted $\Delta^{1,6}$-diester, saponification of diester (II) with 20% NaOH was accompanied by a shift of the double bond from the Δ^1 to the Δ^6 position, which led to 3-methyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (III). The structure of this acid was shown by ozonation with the formation of methylsuccinic acid, and was confirmed by the u. v. spectrum ($\lambda max = 283$ mμ; $\log \epsilon = 3.671$).

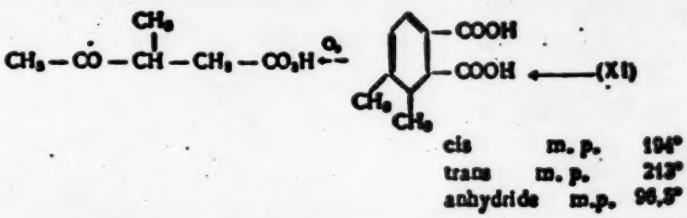
Alkaline saponification of anhydride (I) also proceeded with a shift of the double bond to the Δ^6 position. In this case, however, the reaction was accompanied by a more complex redistribution of the double bonds, and the major product of the conversion was 3-methyl-$\Delta^{3,6}$-cyclohexadiene-1,2-dicarboxylic acid (IV), in which there is a different system of unconjugated double bonds. That this new acid had this structure was proved by the absence of absorption in the u v spectrum, by the ready addition of two moles of hydrogen during catalytic hydrogenation, and by ozonation. It was found that the system of isolated double bonds in acid (IV) is quite stable and does not undergo appreciable transformation during refluxing with a base.



These data show that in 3-methylcyclohexadiene-1,2-dicarboxylic acid, the $\Delta^{1,4}$-system of unconjugated double bonds, which is stable in the presence of an anhydride ring, can isomerize under the rather vigorous conditions of saponification with a shift of the double bond from a position between the carboxyls to the unsubstituted position Δ^{5}. Simultaneously, a shift of the Δ^{4}- bond to the Δ^{3}-position can also take place; however, a further shift of this double bond to the conjugated Δ^{2}-position, a shift which is characteristic of cyclohexadiene-1,2-dicarboxylic acid itself, is hindered by the presence of a methyl group in the 3-position.







This "inhibiting" effect of a methyl group was confirmed with 4-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (V). It was found that the corresponding anhydride (VI) and diester (VII) when refluxed with 20% NaOH gave only the one isomeric acid (VIII) with a $\Delta^{4,6}$ distribution of the double bonds; the structure of this

compound was shown by ozonation and confirmed by the u v spectrum (λ_{max} = 295 mμ; log ε = 3.903). We were unable to obtain products of a more extensive redistribution of the double bonds in this case, the reason apparently being that the methyl group at C_6 was in the way of a possible shift of the second double bond.

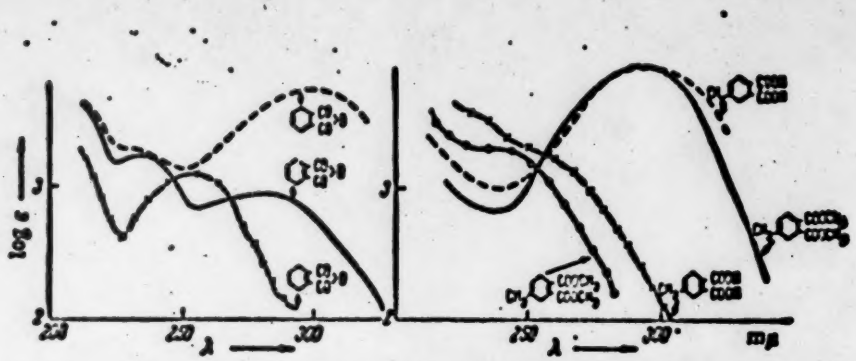
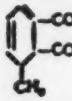
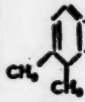


Fig. 1. Typical absorption spectra of the compounds studied.

This same phenomenon was also obtained with 3,4-dimethyl-$\Delta^{1,6}$-cyclohexadiene-1,2-dicarboxylic acid (IX). As in both of the cases described above, the $\Delta^{1,6}$-system of unconjugated double bonds is stable in anhydride (X), but vigorous alkaline saponification of the corresponding diester (XI) led only to 3,4-dimethyl-$\Delta^{1,6}$-cyclohexadiene-1,2-dicarboxylic acid (XII) (or its geometric isomer), the structure of which was proved by ozonation to β-methyllevulinic acid and by the u v spectrum (λ_{max} = 297 mμ; log ε = 3.904). Thus in this case, alkaline isomerization led only to a shift of one double bond from the Δ^1-position to the unsubstituted Δ^6-position, and was not accompanied by isomerization of the second double bond at which there was a methyl group.

TABLE 1*

U V Absorption Spectra of $\Delta^{1,6}$-Cyclohexadiene-1,2-dicarboxylic Acids

Substance	λmax, mμ (C₂H₅OH)	log ε	Compound	λmax, mμ (C₂H₅OH)	log ε
	286	3,780		296	3,908
	288	3,671	 trans cis	297,5 298	3,904 3,799
	285	3,793		308	3,958

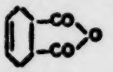
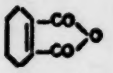
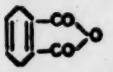
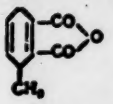
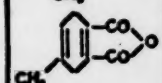
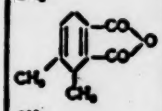
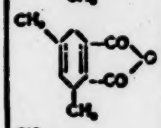
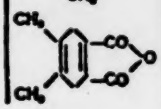
*The u v spectra of all of the compounds shown in the table were taken in our laboratory by T. M. Fadeeva.

The u v absorption spectra of all of the acids containing a conjugated system of double bonds and having the same type of substitution were in agreement. The introduction of a new methyl group at a carbon atom of the conjugated system shifted the absorption maximum approximately 10 mμ toward the long-wave region which is analogous to the well-known Woodward rule [7] (see Table 1).

In the process of proving the structure of our substituted cyclohexadiene-1,2-dicarboxylic acids, interesting spectral regularities were observed for derivatives containing a $\Delta^{1,4}$ double bond system. As would be expected, the dicarboxylic acids and diesters of this series not having a conjugated system of C = C double bonds did not absorb in the 210-300 mμ region. However, the corresponding anhydrides with the same unconjugated distribution of double bonds displayed an anomalous intense absorption in this region. All of them had a characteristic curve with two absorption maximums, one of which was distinguished by a high intensity.

TABLE 2

UV Absorption Spectra of Anhydrides of $\Delta^{1,4}$-Cyclohexadiene-1,2-dicarboxylic Acids

	Anhydride (in acetonitrile)	λ_{max} mμ	Log ε	λ_{max} mμ	Log ε
1		No absorption in the interval 215-250 mμ			
2		255	3,099	—	—
3		238,5	3,250	282,5	2,974
4		240,5	3,443	290	2,874
5		244,5	3,398	290,5	2,838
6		248	3,443	290	2,874
7		248	3,446	288	2,802
8		249,5	3,389	301,5	2,556

The data presented in Table 2 show that when a second, isolated double bond is introduced into the anhydride of a Δ^1-cyclohexene-1,2-dicarboxylic acid, the character of the absorption changes sharply. The peak in the absorption curve of Compound 2, which is characteristic of conjugation of a C = C double bond with the carbonyl groups of the anhydride ring, is considerably shifted in the curve of Compound 3 toward the long wavelength region, and simultaneously there emerges a new absorption maximum which has a rather high intensity in all cases.

The anomalous absorption of anhydrides of $\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acids in the 210-300 mμ region permits the assumption that in these anhydrides there is an electronic interaction of the two formally isolated double bonds, for which homoallylic conjugation [8] is possible as a result of the presence of the rigid system of the five-membered anhydride ring.

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VINYLOXYSILANES

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Until recently, silicon-containing vinyl ethers in which the silicon atom is directly connected to the ether oxygen have been unknown. At the Second All-Union Conference on the Chemistry and Practical Application of Organosilicon Compounds in 1958, S. I. Sadykh-Zade and A. D. Petrov [1] and also N. P. Kharitonov, B. N. Dolgov, and Yu. I. Khudobin [1] presented papers on methods developed by them for the synthesis of compounds of this type.

In the method of S. I. Sadykh-Zade and A. D. Petrov, silicon-containing vinyl ethers are obtained by 1,4-addition of silicon hydrides to α,β-unsaturated aldehydes and ketones in the presence of H_2PtCl_6. N. P. Kharitonov, B. N. Dolgov, and Yu. I. Khudobin synthesized these compounds by catalytic dehydrocondensation of trialkylsilanes with ketones under the influence of alkali metals; those authors consider that the reaction proceeds between the R_3SiH and the enol form according to the schemes

$$R_3SiH + R'C(OH) = R'' \rightarrow R'' = C(R')OSiR_3 + H_2.$$

Only monovinyl ethers are obtained by either the first or the second method. It is impossible in principle to obtain the simplest vinyloxysilanes, $R_3SiOCH = CH_2$, by either the first or the second method.

The considerable difference in the boiling points of isomeric compounds obtained by the two methods merits attention; for example, the boiling point of $(C_2H_5)_3SiOCH = CHCH_3$ is 49-50°/6 mm (S. I. Sadykh-Zade and A. D. Petrov), while that of $(C_2H_5)_3SiOC(CH_3) = CH_2$ is 80°/1 mm (N. P. Kharitonov, B. N. Dolgov, and Yu. I. Khubodin).

For the preparation of vinyl ethers of the type under consideration, we made use of the reaction of mercurated aldehydes and ketones with chlorosilanes.

This reaction proceeds in hydrocarbon or ether medium only with the complete organomercury derivatives of aldehydes and ketones, and it stops at the stage in which the organomercury salt is formed; organosilicon vinyl ethers are obtained in 70-90% yields by this method. The overall equation for the reaction is:

$$n\,Hg(CH_2CHO)_2 + R_{(4-n)}SiCl_n \rightarrow R_{(4-n)}Si(OCH = CH_2)_n + n\,ClHgCH_2CHO,$$

where, in the cases studied, R is CH_3-, C_2H_5-, C_6H_5-, $ClCH_2-$, C_4H_3O-; n is 1, 2, 3, or 4.

The method proposed here permits bonding of from one to four vinyloxy groups to the silicon atom. Vinyloxysilanes are readily hydrolyzed. A crimson color momentarily appears when fuchsin-sulfurous acid is added. Vinyloxysilanes polymerize during storage. The constants, yields, and data from the analyses of the compounds prepared are presented in Table 1.

Proof of structure of our vinyloxysilanes was obtained through the infrared and ultraviolet spectra of triethylvinyloxysilane and triethylisopropenyloxysilane. Absorption bands corresponding to the C = C double bonds were

TABLE 1

Vinyloxysilanes

Compound	Yield, %	B. p., °C/mm	n_D^{20}	d_4^{20}	Found, %			Calculated, %			MR_D	
					C	H	Si	C	H	Si	found	calculated
$(CH_3)_3SiOCH=CH_2$	72	74—75	1,3885	0,7720	51,69	10,47	24,67	51,63	10,41	24,15	35,57	35,20
$(C_2H_5)_3SiOCH=CH_2$	89	53—54/20	1,4275	0,8305	60,72	11,63	17,76	60,70	11,46	17,74	48,99	49,09
$(ClCH_2)(CH_3)_2SiOCH=CH_2$	77	54—55/42	1,4329	0,9796	40,11	7,54	18,56	39,86	7,36	18,64	39,97	40,64
$(ClCH_2)_2CH_3SiOCH=CH_2$	86	73—73,5/14	1,4646	1,1515	32,28	5,49	14,79	32,45	5,44	15,16	44,58	44,88
$(C_2H_5)_2SiOC(CH_3)=CH_2$*	58	65—66/20	1,4290	1,8305	62,32	11,02	16,58	62,72	11,70	16,30	53,12	53,72
$(C_2H_5)_2SiOC(C_2H_5)=CHCH_3$*	63	55—56/3	1,4432	0,8497	65,87	12,11	14,45	65,02	12,07	14,02	62,52	62,08
$(C_2H_5)_2SiOC(C_6H_5)=CH_2$*	45	106—107/3	1,5089	0,9466	71,03	9,05	11,80	71,73	9,46	11,08	73,03	73,48
$(C_2H_5O)_2SiOCH=CH_2$	87	76—77/30	1,3905	0,9493	46,67	8,72	13,89	46,50	8,84	13,68	51,32	51,37
$(CH_3)_2Si(OCH=CH_2)_2$	64	108,5—109	1,4052	0,8792	50,08	8,58	19,16	50,00	8,39	19,47	40,23	40,12
$(C_2H_5)_2Si(OCH=CH_2)_2$	79	69—70/40	1,4240	0,8890	56,16	9,54	16,37	55,78	9,36	16,30	49,52	49,38
$CH_3(C_6H_5)Si(OCH=CH_2)_2$	82	65—66/1,5	1,4940	0,9959	63,83	6,83	13,37	64,03	6,84	13,60	60,21	59,94
$(ClCH_2)(CH_3)Si(OCH=CH_2)_2$	81	72,5—73/30	1,4386	1,0457	40,30	6,27	15,65	40,35	6,21	15,72	44,92	44,96
$CH_3Si(OCH=CH_2)_3$	71	50—51/30	1,4133	0,9457	48,81	7,12	16,28	48,82	7,03	16,29	45,45	45,04
$C_2H_5Si(OCH=CH_2)_3$	76	69—70/40	1,4225	0,9503	51,04	8,02	14,45	51,58	7,58	15,08	49,86	49,67
$C_6H_5Si(OCH=CH_2)_3$	70	79—80/2	1,4896	1,0385	61,54	6,20	11,96	61,50	6,02	11,99	65,19	64,86
$Si(OCH=CH_2)_4Si$	72	52—53/12	1,4146	0,9949	47,89	6,19	14,03	48,02	6,05	14,02	50,36	49,96
$Si[OC(CH_3)=CH_2]_4$*	49	76/5	1,4320	0,9722	56,08	7,98	11,11	56,21	7,86	10,96	68,40	68,48

*Prepared from the organomercury salt of ketones.

found in the i. r. spectra: 1640 cm^{-1} for the first compound and 1650 cm^{-1} for the second. Absorption characteristic of the carbonyl group (280-300 mμ) was not present in the u. v. spectra.

Upon further investigation of the interaction of α-mercurated aldehydes and ketones with chlorosilanes it was found that organomercury salts of oxo compounds also enter into the reaction in the presence of pyridine

$$(C_6H_5)_3SiCl + ClHgCH_2COCH_3 + C_5H_5N \rightarrow (C_6H_5)_3SiOC(CH_3) = CH_2 + C_5H_5N \cdot HgCl_2.$$

When the reaction is carried out by this method with salts of α-mercurated oxo compounds, it is not the triethylchlorosilane that reacts, but its complex with pyridine, $[(C_6H_5)_3Si : NC_5H_5]^+Cl^-$, and, as in the case of such reagents as KI (or KCl) [3], the reaction proceeds at the 1- and 4-positions:

$$ClHgCH_2\overset{\delta+}{C}(=O^{\delta-})-CH_3 \rightarrow CH_2=C(OSi(C_6H_5)_3)-CH_3 + C_5H_5N\cdot HgCl_2$$
$$Cl^-[(C_6H_5)_3Si : NC_5H_5]^+$$

This variant of the reaction permits the use for the synthesis of vinyloxysilanes of the most variegated chloromercurialdehydes and chloromercuriketones, compounds which are much more available than the complete organomercury derivatives of aldehydes and ketones. Starting with salts of α-mercurated oxo compounds, it is possible to prepare organosilicon compounds with different numbers of vinyloxy groups. We synthesized tetraisopropenyloxysilane by this method.

The triethylisopropenyloxysilane synthesized by us had constants very close to those of the isomeric triethylpropenyloxysilane prepared by S. I. Sadykh-Zade and A. D. Petrov and very considerably different from the properties of the compound to which N. P. Kharitonov, B. N. Dolgov and Yu. M. Khudobin assigned the structure of triethylisopropenyloxysilane.

EXPERIMENTAL

1. Preparation of trimethylvinyloxysilane. A solution of 11 g (0.1 mole) of trimethylchlorosilane in 20 ml of isopentane was added, with stirring, to 32 g (0.11 mole) of mercuribisacetaldehyde in 70 ml of isopentane. The mixture was refluxed for 2 hours; the precipitate was then filtered and washed twice with isopentane, and the isopentane was distilled. Distillation of the residue gave 8.4 g (72% of theoretical of trimethylvinyloxysilane with a b. p. of 74-75°, n_D^{20} 1.3885; d_4^{20} 0.7720.

	Found %	: C	51,69;	51,59;	H	10,47;	10,41;	Si	24,67; 24,71
$C_5H_{12}SiO$	Calculated %	: C	51,68;		H	10,41;		Si	24,15

2. Preparation of diethyldivinyloxysilane. A solution of 15.7 g (0.1 mole) of diethyldichlorosilane in 50 ml of absolute ether was added, with stirring, to 64 g (0.22 mole) of mercuribisacetaldehyde in 100 ml of absolute ether. The mixture was refluxed for 2 hours, and the precipitate was then filtered and washed twice with ether. 13.6 g of diethyldivinyloxysilane was obtained by distillation; b. p. 70-71°/40 mm, n_D^{20} 1.4246; d_4^{20} 0.8890.

	Found %	: C	55,79;	55,94;	H	9,43;	9,60;	Si	16,75; 16,37
$C_6H_{14}SiO_2$.	Calculated %	C	55,76;		H	9,36;		Si	16,30

3. Preparation of phenyltrivinyloxysilane. A solution of 10.6 g (0.05 mole) of phenyltrichlorosilane in 20 ml of absolute ether was added, with stirring, to 50 g (0.17 mole) of mercuribisacetaldehyde in 100 ml of absolute ether. The mixture was refluxed for 2 hours, the precipitate was separated, and the filtrate was distilled. 8.2 g (70% of theoretical) of phenyltrivinyloxysilane was obtained; b. p. 79-80°/2 mm, n_D^{20} 1.4896; d_4^{20} 1.0385.

	round %:	C	61,40;	61,54;	H	6,12;	6,20;	Si	12,26; 11,98
$C_{12}H_{14}SiO_2$.	Calculated %:	C	61,50;		H	6,02;		Si	11,99

4. Preparation of tetravinyloxysilane. A solution of 17 g (0.1 mole) of silicon tetrachloride in 50 ml of isopentane was added, with stirring, to 120 g (0.42) mole of mercuribisacetaldehyde in 150 ml of isopentane. The reaction mixture was refluxed for 2 hours, the precipitate was removed by filtration, and the solvent was distilled under vacuum. There was obtained 14.3 g (72% of theoretical) of tetravinyloxysilane with a b. p. of 52-53°/13 mm, n_D^{20} 1.4146; d_4^{20} 0.9949.

	Found %	: C 48.21;	47.89;	H 6.38;	6.12;	Si 13.97; 14.08
$C_8H_{12}SiO_4$.	Calculated %	: C 48.02;		H 6.05;		Si 14.02

5. Preparation of tetraisopropenyloxysilane. 32 g (0.4 mole) of pyridine was added to 125 g (0.42 mole) of chloromercuriacetone in 250 ml of benzene, and to this mixture was added, with stirring, a solution of 17 g (0.1 mole) of silicon tetrachloride in 30 ml of benzene. The reaction mixture was refluxed for 1.5 hours, the precipitate was separated, the solvent was distilled, and the residue was distilled under vacuum. There was obtained 12.5 g (49% of theoretical) of tetraisopropenyloxysilane with a b. p. of 76/5 mm; n_D^{20} 1.4320; d_4^{20} 0.9722.

	Found %	: C 58.08;	58.41;	H 7.93;	8.13;	Si 11.11; 10.90
$C_{12}H_{20}SiO_4$.	Calculated %:	C 58.21;		H 7.88;		Si 10.98

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THE SYNTHESIS OF ESTERS OF CARBOXYLIC ACIDS FROM CARBON MONOXIDE, CYCLOOLEFINS, AND ALCOHOLS

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(Presented by Academician B. A. Kazanskii, June 3, 1959)

We have previously reported [1] on a new route for the synthesis of esters of carboxylic acids from carbon monoxide, olefins, and alcohols. The synthesis is carried out in two stages using concentrated sulfuric acid as the catalyst. It was shown* that the major product obtained from normal C_5-C_7 α-olefins are alkanoic acids having one more carbon atom than the original olefin and containing two methyl radicals in the molecule in the α-position. The ester of the isomeric acid containing an ethyl radical in the α-position is also obtained, though in lower, but all the same significant yield. Acyl sulfuric acids (mixed anhydrides of sulfuric acid and the carboxylic acids) are formed from the carbon monoxide, olefin, and sulfuric acid in the first stage as intermediate products, and these acylate the alcohols in the second stage.

The present paper briefly presents the experimental data obtained in an investigation of the carbomethoxylation and carboethoxylation of cyclopentene and cyclohexene by the method indicated.

TABLE 1

Synthesis of Esters of Cycloolefins C_5-C_6

Expt. No.	Used, ml			CO absorbed		Yield of ester		
	cycloolefin	alcohol		liters	% of theoretical	ml	% of absorbed CO	% of original olefin
1	Cyclopentene 250	Methyl	300	27,8	44,5	90	54,0	23,8
2	Cyclopentene 185	Ethyl	250	21,8	45,3	64	44,3	20,0
3	Cyclohexene 300	Methyl	300	50	75,0	215	67,2	50,8
4	Cyclohexene 300	Ethyl	300	50	75,0	215	60,0	45,0

EXPERIMENTAL

The first stage of the process – the interaction of CO, H_2SO_4, and cycloolefin – was carried out at 20-40° and an initial carbon monoxide pressure of 80 atm in a stainless steel autoclave fitted with a stirrer turning 800 revolutions per minute and an inlet tube for the cycloolefin. The methyl or ethyl alcohol was added to the reaction mixture in the second stage. The resulting mixture of esters was distilled from a Favorskii flask at a pressure of 3 mm Hg, and was then fractionated in a column with an efficiency of 90 theoretical plates. From

*Report given at The VIII Mendeleev Conference on General and Applied Chemistry [2].

the fractions corresponding to the individual esters were prepared the anilides of the acids, from which the esters were identified. The anilides were prepared by reacting the ester with anilinemagnesium bromide [3]. Mixtures of anilides obtained from the methyl and ethyl esters of the same acid melted without depression of the melting point. The initial cyclopentene (b. p. 44-45°/760 mm, d_4^{20} 0.7717, n_D^{20} 1.4228, bromine number 223.5) was prepared in 60% yield by hydrogenation of cyclopentadiene in an autoclave at room temperature and a pressure of 80 atm over Raney nickel [4]. The initial cyclohexene (b. p. 83.2-83.3°/760 mm, d_4^{20} 0.8106, n_D^{20} 1.4468, bromine number 193.5) was synthesized in about 80% yield by dehydration of cyclohexanol in the presence of concentrated sulfuric acid [5].

TABLE 2

Esters Prepared from C_5-C_6 Cycloolefins, Carbon Monoxide, and Methyl or Ethyl Alcohol

Initial cycloolefin	Acid	B. p., °C at 760 mm	d_4^{20}	n_D^{20}	M. p. of anilide
		Methyl ester			
Cyclopentene	Cyclopentanecarboxylic	158,2	0,9859	1,4360	160,5
	1-Methylcyclopentane-1-carboxylic	163,0	0,9654	1,4384	107
Cyclohexene	Cycloxanecarboxylic	181,1—181,3	0,9785	1,4438	148
		Ethyl ester			
Cyclopentene	Cyclopentanecarboxylic	174,1	0,9583	1,4343	160,5
	1-Methylcyclopentane-1-carboxylic	176,9—177,2	0,9393	1,4327	107
Cyclohexene	Cycloxanecarboxylic	196,0—196,2	0,9549	1,4413	148

Data from the experiments on the syntheses and their results are presented in Tables 1 and 2. A mixture of esters which contained about 40-50% of the methyl and ethyl esters of cyclopentanecarboxylic acid was obtained from cyclopentane in a yield of about 45-55% based on the CO absorbed and of 20-24% based on the original cyclopentene. The literature value for the b. p. of the ester of this acid is 172-174°/752 mm [6], and the melting point of the anilide of the acid is 160.1-160.2° [7].

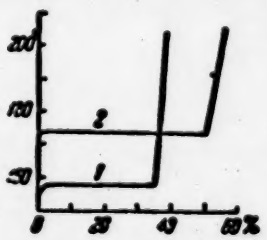
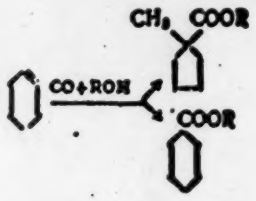


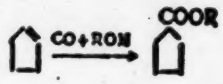
Fig. 1. Distillation curves of esters prepared from cyclopentane. Esters of cyclopentanecarboxylic acid: 1) methyl, 2) ethyl.

Fig. 2. Distillation curves of esters prepared from cyclohexene. a) Esters of 1-methylcyclopentane-1-carboxylic acid: 1) methyl, 2) ethyl; b) esters of cyclohexanecarboxylic acid: 1) methyl, 2) ethyl.

A mixture of the methyl and ethyl esters of two acids – 1-methylcyclopentane-1-carboxylic acid (60%) and cyclohexanecarboxylic acid (40%) – was obtained from cyclohexene in a yield of 60-67% based on the carbon monoxide absorbed and of 45-51% based on the original cyclohexene. Literature data for the methyl ester of 1-methylcyclopentane-1-carboxylic acid are: b. p. 139.5°/721 mm [8], d_4^{20} 0.9641, $n_D^{19.5}$ 1.4373, m. p. of the anilide of the acid 105° [9]; the literature value for the boiling point of the methyl ester of cyclohexanecarboxylic acid is 181-182° [10]; the literature value for the b. p. of the ethyl ester is 196.5°/760 mm [11], and the literature value for the anilide of the acid is 145-146° [12]. Thus, a skeletal isomerization similar to that which occurs during the synthesis of esters from α-olefins occurred during the synthesis of esters from cyclohexenes; i. e., in addition to esters of cyclohexanecarboxylic acid, there were obtained esters of a carboxylic acid in which the carboxylic group was attached to a quaternary carbon atom.



Esters of only a single acid were isolated from the reaction products of cyclopentene; these were formed by direct carboxylation of the cycloolefin without skeletal isomerization.



However, the yield of esters was 2-3 times lower than usual, and a large part of the cyclopentene was converted to high-boiling products.

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SYNTHESIS OF HYDROCARBONS OF THE INDANE SERIES

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The majority of the publications devoted to the synthesis of alkylindanes describe either a method based on Grignard synthesis or a complex preparative method based on closure of the five-membered ring with subsequent reduction of the resulting indanone [1, 2, 3]. In only a few cases has alkylation of the indane been used for the introduction of alkyl side chains into the aromatic ring [4-7]. In a number of cases, this last method gave completely satisfactory results, and this method has also been used in the present work for the preparation of some indanes with substituents in the aromatic ring.

The starting material for these synthesis – indane – was prepared by hydrogenation of indene over a Raney nickel catalyst at a pressure of 120-150 atm at ordinary temperature [8]; the resulting indane had a b. p. of 172° at 750 mm, n_D^{20} 1.5389, and d_4^{20} 0.9617, which are in agreement with the literature values [9]. During the alkylation reaction, the reaction mixture was stirred mechanically and was cooled with ice water. The reaction products were separated in the usual manner, and the major fraction of these products was distilled 2-3 times in a Fenske-type column having an efficiency of 12 theoretical plates. The location of the side chains was established by means of ultraviolet absorption spectra, which were obtained in the Laboratory of Petroleum Physics and Physical Chemistry of the Institute of Petrochemical Synthesis of the Academy of Sciences USSR by M. V. Shishkina; these spectra showed that in all of the monosubstituted indanes, the side chain was in the 5-position.

5-Tert-butylindane was prepared by passing isobutylene into indane while gradually adding 96% sulfuric acid. The starting materials were used in the amounts required to give a molar ratio of indane to isobutylene to sulfuric acid of 2:1:1. The hydrocarbon was obtained in a yield of 48%, calculated on the isobutylene. A total of 170 g of indane was introduced into the reaction.

$C_{13}H_{18}$.	Found %	C 89,56;	89,48;	H 10,40;	10,43
	Calculated %	C 89,58;		H 10,42	

Mol. wt.: found, 174 and 174; calculated, 174.

The constants of the tert-butylindane, together with those of all of the other hydrocarbons prepared, are presented in Table 1. This hydrocarbon has previously been prepared by alkylation of indane with tert-butyl chloride in the presence of aluminum chloride, but the characterization of it was totally insufficient.

5-Heptylindane was prepared by the interaction of indane with heptene and sulfuric acid, the reagents being used in a molar ratio of 2:1:1. 140 g of indane was introduced into the reaction. The heptane was prepared by dehydration of n-heptyl alcohol at 370° over aluminum oxide. A fraction with a b. p. of 95° at 742 mm, n_D^{20} 1.4050, and d_4^{20} 0.7020 was obtained in this experiment. When 96% sulfuric acid was used, the yield of the basic heptylindane fraction was 20%; when a more dilute acid (92%) was used, the yield increased to 70% (based on the heptene).

$C_{16}H_{24}$.	Found %	C 88,77;	88,81;	H 11,28;	11,17
	Calculated %	C 88,82;		H 11,18	

Mol. wt.: found, 214 and 221; calculated, 216.

5-Octylindane was prepared from 2-ethylhexene, which was synthesized by dehydration of 2-ethylhexyl alcohol at 370° over aluminum oxide and which had a b. p. of 117-119° at 732 mm, n_D^{20} 1.4173, d_4^{20} 0.7252. The interaction of this hydrocarbon with indane proceeded under the influence of 90% sulfuric acid at a molar ratio of indane to octene to sulfuric acid of 2 : 1 : 1. 147 g of indane was introduced into the reaction. The yield of alkylation product was 47% (based on the octene).

$C_{17}H_{26}$. Found %: C 88.57; 88.62; H 11.37; 11.40
Calculated %: C 88.62; H 11.38

Mol. wt.: found, 225 and 226; calculated 230.38. When this reaction was carried out in the presence of aluminum chloride, the yield was only 14%.

The cyclopentylindane and dicyclopentylindane described in the literature was synthesized by Cagniant and co-workers [5] from indane and cyclopentene under the influence of aluminum chloride. We repeated this synthesis with the aim of obtaining a more detailed characterization of these hydrocarbons; it was also desired to

TABLE 1

Properties of Indane Hydrocarbons

Hydrocarbon	B. p., °C/mm Hg	F.p., °C (in glass)	d_4^{20}	n_D^{20}	Viscosity, centistokes, at indicated temp., °C					Aniline point (max), °C
					20	30	50	70	100	
5-Tertiarybutylindane, $C_{13}H_{18}$	241.5/752 85.5—86/4	—70	0.9288	1.5235	5.1	3.7	2.4	1.8	1.2	—10
5-Heptylindane, $C_{16}H_{24}$	283—284/736 120.5—121.5/3.5	—60	0.9130	1.5130	11.1	7.8	4.3	2.9	1.7	—3.5
5-Isooctylindane, $C_{17}H_{26}$	297.5/742 121—122/2	—60	0.9221	1.5188	25.9	15.3	6.9	4.3	2.2	+2
5-Cyclopentylindane, $C_{14}H_{18}$	286.5/742 100—102/2	—70	0.9904	1.5493	7.5	6.8	4.9	3.8	1.4	—14
Dicyclopentylindane, $C_{19}H_{26}$	336—337/736 179—181/4	—6	1.0066	1.5567	68.5	40.6	16.2	8.9	4.2	—13
Tricyclopentylindane, $C_{24}H_{34}$	210—212/3	+17	1.0110 (40°)	1.5622	—	—	—	—	—	—
1-Cyclopentylindane, $C_{14}H_{18}$	279—280.5 113—114/3.5	—63	0.9903	1.5434	—	—	—	—	—	—14

obtain tricyclopentylindane, a compound which has not been described in the literature. 100 g of indane was reacted with 19 g of cyclopentene (molar ratio of 3 : 1) in the presence of 10 g of aluminum chloride; the reaction products were twice distilled in the column, and two fractions were obtained. The yield of the fraction boiling at 117-118° at 4 mm was ~40%.

$C_{19}H_{26}$. Found % : C 90.28; 90.23; H 9.91; 9.87
Calculated % : C 90.28; H 9.76

Mol. wt.: found, 183 and 183; calculated, 188.

The yield of the fraction boiling at 179-181° at 5 mm was ~20%.

$C_{19}H_{26}$. Found %: C 89.48; 89.46; H 10.57; 10.60
Calculated %: C 89.69; H 10.31

Mol. wt.: found, 247 and 247; calculated, 254.4.

It was established by ultraviolet spectroscopy that the cyclopentyl ring in the cyclopentylindane was at the 5-position.

Tricyclopentylindane was prepared by alkylating with cyclopentene the broad fraction boiling at 113-120° at 3 mm separated from the products of the condensation of indane with cyclopentene; this fraction was a mixture of mono- and dicyclopentylindanes. 55 g of the braod fraction, 40 g of cyclopentene, and 10 g of aluminum chloride were charged to the reaction, which was carried out in cyclohexane solution. A fraction boiling at 210-215° at 3 mm was separated from the reaction products by vacuum distillation.

$C_{23}H_{34}$.	Found %:	C 89,40; 89,52; H 10,02; 10,65
	Calculated %:	C 89,37; H 10,63

Mol. wt.: found, 309; calculated, 322.

It is interesting to note that tricyclopentylindane is a very viscous liquid, while its analog with three cyclohexyl groups – tricyclohexylindane – is a solid with an m. p. of 115° [7].

In order to compare the properties of 5-cyclopentylindane with the properties of its isomer in which the cyclopentyl group is attached to the five-membered ring, we synthesized 1-cyclopentylindane. For this purpose, we used a synthesis in which indene is condensed with ketones; this synthesis was developed by Thiele [11] for the preparation of benzofulvenes, and was used, in a somewhat modified form, by Ruzicka and Peyer [12]. This reaction, still more modified, was used by us for the synthesis of certain indane homologs [13]. It is necessary to point out that while in the synthesis of hydrocarbons of the indane series with alkyl groups attached to the five-membered ring, the reaction in which the corresponding intermediate diene hydrocarbon is prepared can be carried out without the use of ether as a solvent; in the case of cyclopentanone, this reaction proceeds only in ether solution. 100 g of indene was introduced into the reaction of indene with cyclopentanone, which was carried out with molar amounts of the starting materials. The yield of the intermediate product was ~24% (based on the indene); this product was a broad fraction of diene hydrocarbon boiling at 116-130° at 2.5 mm, and was a yellow, crystalline material under ordinary conditions.

$C_{18}H_{18}$.	Found %:	C 92,33; 92,23; H 7,71; 7,74
	Calculated %:	C 92,25; H 7,75

The hydrogenation of this hydrocarbon was carried out over Raney nickel catalyst at ordinary temperature and an initial hydrogen pressure of 125 atm. 14 g of a colorless hydrocarbon was obtained by distillation of the reaction products.

$C_{18}H_{22}$.	Found %:	C 90,30; 90,31; H 9,74; 9,77
	Calculated %:	C 90,28; H 9,74

Mol. wt.: found, 185 and 187; calculated, 188.

In addition to the tricyclopentylindane, we have also prepared for the first time 5-heptylindane, 5-isooctyl indane, and 1 cyclopentylindane.

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ON "DEVIATIONS" FROM RAOULT'S LAW

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(Presented by Academician V. A. Kargin, May 21, 1959)

In a preceding article [1], we considered "deviations" from Raoult's law when the law is applied to the vapor pressure of a binary system, the components of which chemically interact. In the present article, we shall consider yet another reason for "deviations" of vapor pressure from Raoult's law, and we shall also show how these reasons are reflected in melting diagrams and in the calculation of molecular weight from cryoscopic measurements.

Let us assume that one of the components of our binary system is a dimer and that the system obeys Raoult's law. Let us further assume that in the construction of the vapor pressure-composition diagram of our system, as is usual in such cases, we use in the calculation of the mole fractions of the associated component A its formula molecular weight; i. e., we carry out the calculation on the monomer. In this case, the diagram will have the form shown in Fig. 1. This diagram shows "deviations" of the vapor pressure from Raoult's law, although in actuality there are no deviations (as assumed), and the vapor pressure (partial and total) is not represented by straight lines, solely because we used in the calculations an incorrect molecular weight for component A.

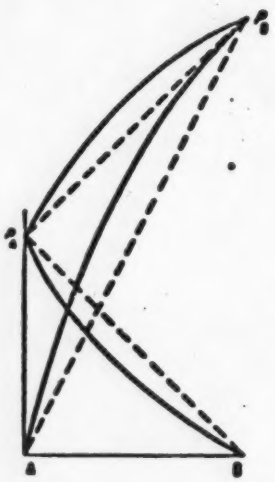

Fig. 1. Vapor pressure of the binary system A – B; component A is a dimer.

In the construction of the diagram (Fig. 1), we assumed that we were dealing with a dimer which does not decompose upon dilution with the inert component B. In the event that this condition is not fulfilled but the dissociation constant of the dimer molecules is ordinarily small, the diagram will differ only in that all of the vapor pressure curves will converge to additive straight lines close to the B coordinate.

Let us consider now what form the melting diagram will have for a system in which chemical interaction occurs and for a system in which there is no chemical interaction but in which there is an associated component. For this purpose, we shall assume, as before, that our systems obey Raoult's law and that the liquidus curves for the components of our systems are described by the Schroeder–Le Chatlier equation.

We must take into consideration that the composition of the initial mixture enters into the construction of the diagram and that the temperature of initial crystallization of a component depends on its mole fraction, which changes from x, as a result of the reaction $m\,A + n\,B = A_mB_n$, to $(x-my)/[1-(m+n-1)\,y]$, where y, as before [1], is the number of moles of the compound A_mB_n formed per mole of the original mixture.

Taking this change in the mole fractions into account, we constructed liquidus curves for the substance A for different interactions with the second component B.

In Fig. 2, Curve I represents "ideal" solubility of our component A (interaction is absent; $y = 0$); in the

case in which the compound AB is formed (there is interaction which proceeds to completion), Curve II is obtained; Curve III corresponds to the formation of A_2B*.

If compound AB_2 is formed, then as a result of the interaction, the mole fraction of component A increases in comparison to the original, and the temperature of initial crystallization (Fig. 3, Curve II) lies above the "ideal" Curve I (Fig. 3) from x = 1 to x = 0.5. In the case where component B is associated (dimerized) but does not interact with A, Curve III of Fig. 3 is obtained. The latter lies above the "ideal" Curve I over its entire extent, but Curve II intersects Curve I at x = 0.5. Curve II of Fig. 4 intersects Curve I at this same point (x = 0.5), which corresponds to the formation of the compound A_2B_3. However, Curve II of Fig. 4 does not coincide with Curve II of Fig. 3, but merely intersects it at the point x = 0.5. From pure component A to this point, the curve corresponding to the formation of compound A_2B_3 lies above the curve corresponding to the compound AB_3, while after this point it lies below.

Fig. 2.

Certain practical consequences relating to the cryoscopic determination of molecular weight follow from a consideration of the curves presented in Figures 2, 3, and 4.

Analysis of the Schroeder-Le Chatlier equation, in which the equilibrium concentration of component A appears in place of its initial concentration, shows the following. If component A is the cryoscopic solvent in which the determination of the molecular weight of B is carried out, and if A and B react according to the equation $mA + nB = A_mB_n$, then the results of the determination of the molecular weight of B uniquely depend on n – the stoichiometric coefficient of the equation for the reaction.

If the reaction forming A_mB_n proceeds irreversibly (to completion), then the slope of the tangent to the corresponding curve at the point T_A is 1/n times the slope of the tangent to the "ideal" Curve I at this same point (Figures 2, 3, and 4). This implies that the cryoscopic determination of the molecular weight of B leads to values which are n times the true value.

Consequently, for n = 1, the correct value of the molecular weight of B must be obtained in spite of interaction of B, the substance tested, with the cryoscopic solvent, A. Actually, in Fig. 2 all three curves have a common tangent at the point T_A. Therefore, when the determination of the freezing point of A is carried out at sufficiently low concentrations of B, we obtain the true value of the molecular weight.

Fig. 3.

In Fig. 3, II and III have a common tangent at the point T_A. The slope of this tangent is equal to half of the slope of the tangent of Curve I. This means that cryoscopic determination of the molecular weight of B will yield a value which is twice the true value not only when B actually is a dimer (curve III), but also in the case when the monomeric substance B forms a compound having the composition AB_2 with the cryoscopic solvent A. Thus, by carrying out measurements in solutions which are very dilute with respect to B, it is possible to determine with which of two cases (B_2 or AB_2) we are dealing. For a solution to this problem, it is necessary to continue the measurements to higher concentrations of B.

In the case of the formation of the compounds A_2B_3 and AB_3, cryoscopic determination of the molecular weight of B yields values which are three times the true value, since Curves II and III (Fig. 4) have at the point T_A a common tangent whose slope is one-third the slope of the tangent to Curve I.

*T. N. Sumarokova [2] established similar relationships by a consideration of experimental data.

Fig. 4.

We emphasize once more that all of our calculations were carried out with the assumption that the systems under consideration obey the law for ideal solutions; i. e., it was assumed that the activity coefficients of all substances participating in the equilibriums considered are 1 at all concentrations. Thus, the "deviations" from the laws of ideal solutions which we have discussed are apparent deviations, since all calculations were carried out with the assumption that these laws are obeyed.

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THE MECHANISM OF THE OSAZONE-FORMATION REACTION

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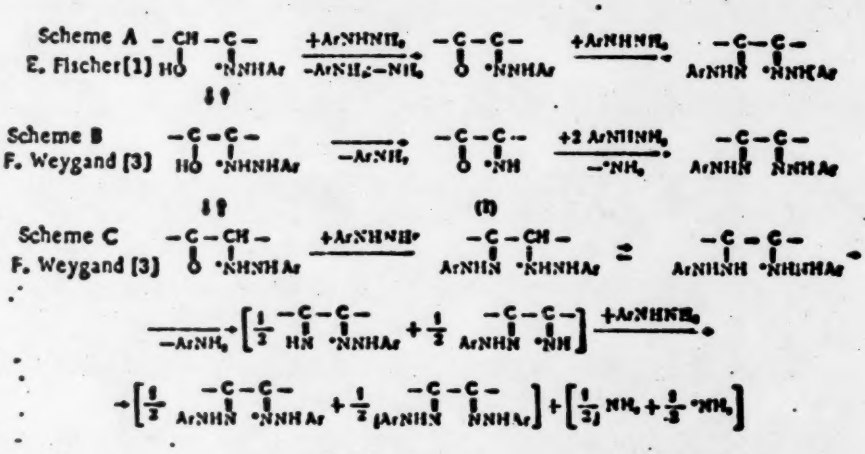
In spite of a considerable number of investigations [1-15], the mechanism of the formation of osazones from α-hydroxycarbonyl compounds remains obscure. All of the hypotheses and ideas regarding this problem which have been published up to the present can be reduced to three schemes – A, B, and C.

We considered that the question of which of these schemes is correct can be decided with the aid of N^{15}. As a matter of fact, if a β-N^{15}-hydrazone is acted on by unlabeled arylhydrazine, then in this case the content of N^{15} in the final products – osazone and ammonia – will depend on which of these schemes is followed in osazone formation (in the schemes below, $N^{15} = N^*$).



Indeed, if Scheme A is correct, the ammonia should not contain excess N^{15}, which will be found wholly in the osazone. In the event that Scheme B is correct, the osazone will be unlabeled, and the ammonia will contain all of the tagged nitrogen. Finally, if Scheme C is correct, the excess N^{15} should be distributed equally between the osazone and the ammonia.

Unfortunately, a study of the mechanism of osazone formation by means of tagged atoms is faced with considerable difficulty owing to the possible dilution of the labeled group in the osazone or hydrazone through exchange of a labeled (unlabeled) hydrazine group for an unlabeled (labeled) group by hydrolysis or direct replacement. However, these side processes may successfully be eliminated to a considerable extent by forming the osazone in boiling isoamyl alcohol with simultaneous removal of the water from the sphere of the reaction. Under these conditions, dilution of the labeled group in the hydrazone does not initially attain any great value and does not obscure the mechanism of osazone formation. Therefore, by stopping the reaction after a specific

time interval (depending on the nature of the hydrazone used), it is possible to judge with sufficient accuracy from the distribution of the tagged atom between the initial and final compounds which of the three proposed schemes is actually followed.

The investigations were carried out with β-N^{15}-p-nitrophenylhydrazones of fructose, cyclohexanolone, and benzoin. Boiling alcoholic solutions of β-N^{15}-hydrazone and of unlabeled p-nitrophenylhydrazine (2 moles) were combined and then refluxed in a stream of nitrogen, so that the resulting ammonia was immediately removed

TABLE 1

Expt. No.	Original β-N^{15}-hydrazone (39.6 atom % N^{15})	Reaction time, min	N^{15} content in atom %		
			in ammonia	in β-N-atom of the unreacted hydrazone	in β-N-atom of the unreacted hydrazine
1	Fructose	10	35.8	32.2	3.8
2	"	60	20.4	–	–
3	Cyclohexanolone	5	23.4	23.8	7.9
4	"	20	16.5	–	–
5	Benzoin	360	39.0	39.4	0.68

from the reaction mixture. At the conclusion of the heating period, the separation of the compounds from the reaction mixture and the isolation of the osazone, hydrazone, and hydrazine were carried out as rapidly as possible in order to eliminate further change in the labeling through exchange. Such change was not, however, completely eliminated; consequently, it was expedient to measure the isotope composition of the ammonia instead of that of the osazone.

As may be seen from the data presented in Table 1, the evolved ammonia initially always contained significantly more than half of the tagged nitrogen of the original hydrazone; whence, it follows that in all of the cases investigated, the process of osazone formation proceeds according to Scheme B*. It is important that there was quite good conformity of the contents of tagged nitrogen in the ammonia, the unreacted hydrazone, and the unreacted hydrazine**, which indicates that osazone formation was not accompanied by any other reactions except the exchange between the labeled hydrazone and the unlabeled hydrazine.

Scheme B is distinguished from the other two schemes by the fact that the first stage of the reaction proceeds without the participation of the hydrazine. This provided basis for the hope that the process of osazone formation could be separated into two stages with isolation of the intermediate monoimine of α-diketone (I). In fact, when benzoin p-nitrophenylhydrazone was used, we noted that during prolonged heating at 60° in glacial AcOH in the absence of a hydrazine, it gradually disappeared, and then upon subsequent addition of two moles of hydrazine, a precipitate of the osazone rapidly formed. When cyclohexanolone p-phenylhydrazone was heated in glacial acetic acid in the presence of 2.2 moles of Ac_2O (60°, 1 hour), it was possible to isolate, along with the p-nitroacetanilide (80%), the N-acetyl derivative of the corresponding monoimine of the α-diketone (m. p. 63°, from ether; 30 % yield),

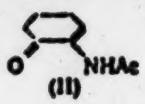
$C_8H_{11}O_2N$. Found %: C 62.77; H 7.47; N 9.20;
Calculated %: C 62.72; H 7.24; N 9.15

which is direct proof that Scheme B is correct.

* The former conclusion [13] that Scheme C is correct in the case of benzoin was in error.

** The contents of N^{15} in the ammonia and the unreacted hydrazone were approximately the same, and the sum of the N^{15} in this hydrazone and twice the content of excess N^{15} in the unreacted hydrazine was close to the content of N^{15} in the original hydrazone.

A study of the infrared spectrum showed that the compound isolated had the structure of an enamine (II).



(II)

With p-nitrophenylhydrazine it gave the corresponding hydrazone (m. p. 217°, from MeOH).

Found %: C 58.35; H 5.67; N 19.38;
$C_{14}H_{16}O_3N_4$. Calculated %: C 58.32; H 5.50; N 19.44

and when heated with an excess of this hydrazine in 1 N HCl, AcOH, NH_3, and the osazone of cyclohexanolone were formed.

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ORIENTATION OF MASSIVE POLYMERIC MATERIALS

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Linear polymers in massive form such as blocks, sheets, etc., polymers such as, for example, polymethyl methacrylate, polystyrene, etc., frequently have insufficient strength and, in particular, plasticity, and as a consequence they have an increased susceptibility to concentrated loads and unsatisfactory properties with respect to impact tests. These flaws of such materials hamper their use in engineering and frequently make their application quite impossible.

In this connection, there has existed for a long time a tendency to solve new technical problems, particularly those of mechanical engineering, through the synthesis of all-new polymers and new polymers with the required properties.

Moreover, it has long been known that polymeric fibers and films prepared by methods leading to orientation of the macromolecules have higher strength and of particular importance, better plastic characteristics [1-7].

The positive side of this method of polymer modification is that, without a change in the chemical composition of the polymer or the technology of its preparation, it is possible to obtain a new material having the desired properties by changing the degree of orientation; in addition, special additives may be used to prevent extensive cross-linking or to provide other effects. Hence, it appeared to be necessary to resolve the question of the expediency of orienting massive polymeric materials and also to develop commercially feasible methods for their orientation. Bartoe has reported on the application of oriented polymethyl methacrylate to aviation problems without describing the method used for its preparation [8]. After testing a large number of laboratory methods for the preparation of oriented massive polymeric materials, we have developed two methods for the production of such oriented materials, methods which have excellent prospects; one of these methods depends on polyaxial drawing, while the other is based on pressing. A special machine was developed for the production of oriented polymethyl methacrylate by the drawing method (see Fig. 1); such material is useful, for example, for glassing aircraft cabins.

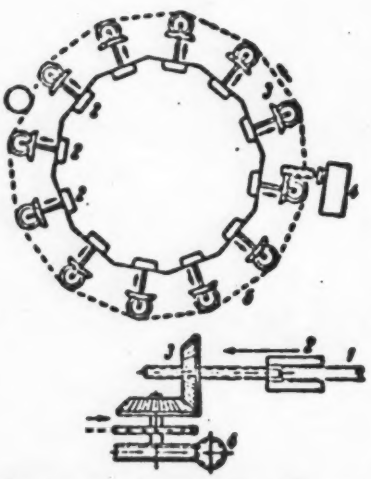

Fig. 1. Schematic drawing of the machine for the production of oriented organic glass: 1) polymer, 2) clamp, 3) drawing assembly, 4) reducer, 5) chain.

This machine produces oriented polymethyl methacrylate by drawing it in 12 radial directions. The drawing is carried out at a temperature at which the material is in a highly elastic state.

This machine will produce sheets of polymethyl methacrylate having a thickness of 10-15 mm and a diameter of up to 2 meters, the degree of drawing being of the order of 30% per pass. The basic element of this machine is the drawing assembly, which consists of a pair of conical gears, one of which acts as a threaded

member which, when rotated, gives a forward motion to the screw holding the clamp. There are twelve such assemblies distributed around the circumference of a stiff frame and connected through sprockets to a chain drive; this arrangement guarantees simultaneous uniform drawing in twelve directions. One of the twelve assemblies is connected to a worm reducer, and acts as the drive for the entire apparatus.

In addition to the apparatus in which massive polymeric materials are drawn, we also developed a method employing compression. In this method, orientation of polymers is accomplished by means of presses. This method produces sheets of polymethyl methacrylate having dimensions of 750 x 25 mm, which are useful for special purposes. Polymethyl methacrylate blocks having a thickness of 50-80 mm, heated to a temperature such that they are in a highly elastic state, are placed between the plates of a press and pressed to the required degree of compression; they are then cooled under pressure. It was found that the required specific pressure increases with an increase in the degree of compression. The greater the dimensions of the initial stock, the higher is the required specific pressure for a corresponding degree of compression.

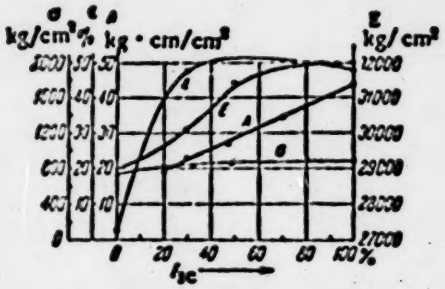

Fig. 2. Dependence of the modulus E, tensile strength σ and elongation ε, and specific resilience A, on degree of orientation.

A special lubricant was applied to the plates of the press, so that the organic glass [polymethyl methacrylate] would slide more freely over the plate surface. In order for the polymethyl methacrylate to retain its original transparency, it was necessary to carry out the pressing operation between plates made from a high-strength, tempered, and polished silicate glass. One measure of the degree of orientation of massive polymeric materials at specific temperature regimes is the degree of stretching or compression determined from the equation $E_{sc} = (\sqrt{T_1/T_2} - 1) \cdot 100$, where E_{sc} is the degree of stretching or compression in per cent, T_1 – is the original thickness of the polymer sheet in mm, T_2 – is the final thickness of the polymer sheet in mm. This equation was developed from an equation expressing the change in volume before and after stretching or compression. Data illustrating the physicomechanical properties of oriented polymethyl methacrylate prepared by stretching and by pressing are shown in Table 1. It follows from these data that at equal degrees of stretching or compression,

TABLE 1

	Tensile strength during elongation, kg/sq. cm	Elongation %	Modulus, kg/sq. cm	Compressive strength, kg/sq. cm	Brinell hardness, kg/sq. cm	Specific resilience, kg · cm/sq. cm
Pressing	792	20.6	25450	1251	22.9	24.8
Drawing	763	21.5	26100	1275	22.8	24.9

the indices of the physicomechanical properties of the oriented polymer prepared by the two methods are practically the same. The degree of stretching or compression depends on the required properties of the oriented material.

Figure 2 shows the dependence of modulus, tensile strength, elongation, and specific resilience on the degree of orientation. It follows from these data that an increase in the degree of drawing above 50-70% leads to practically no further improvement in the properties of oriented polymethyl methacrylate, except for the specific resilience. Figure 3 shows the dependence of the physicomechanical properties of oriented (E_{sc} of the order of 50%) and unoriented polymethyl methacrylate on the test temperature. From these data it follows that the indices of physicomechanical properties, for example, specific resilience, elongation at break, and others characterizing the plasticity of the material, are significantly higher for oriented than for unoriented polymethyl methacrylate over a broad temperature interval from –60° to the temperature at which deorientation begins (10-12° below the

softening point). The specific resilience of the oriented polymethyl methacrylate was more than twice as high as that of the unoriented polymer over the entire temperature range investagated. The elongation at break of the oriented material at temperatures below zero and at ordinary temperatures also significantly exceeded that of the unoriented polymer. At elevated temperatures close to the glass temperature of polymethyl methacrylate, the difference between the elongations at break of the oriented and unoriented material decreased.

The physicomechanical indices characterizing the strength and stiffness of the material, for example, the tensile strength and modulus, were higher for oriented polymethyl methacrylate than for unoriented at normal temperatures and temperatures below zero, but at higher temperatures these indices for the oriented and unoriented polymethyl methacrylate were about on the same level, and that of the oriented polymer was even somewhat lower. However, as shown by experiment, the static strength of, for example, aircraft parts, made from the oriented polymethyl methacrylate was twice and more as high as that of parts made from the unoriented polymer. This is explained by the high value of the work required to cause failure in oriented organic glass, which, in turn, is a consequence of the high plasticity of this material, its high resistance to bursting, its low susceptibility to concentrated loads and, of particular importance, its ability to withstand considerable deformation without any signs of failure. Figure 4 presents curves showing the dependence of brittle strength and impact elastic limit on temperature. It follows from these data that the appreciable increase in brittle strength in conjunction with a small increase in impact elastic limit sharply increased the temperature interval over which plastic deformation occurred. The brittle temperature of the oriented polymer at a high degree of drawing was 80-90° lower than that of the unoriented polymer.

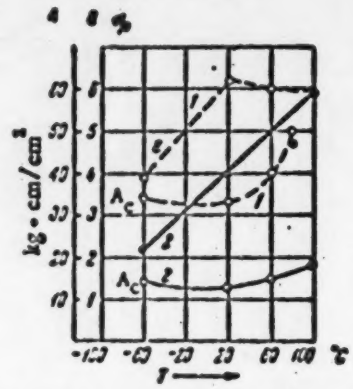

Fig. 3. Dependence of specific resilience A, and elongation at break ε, of oriented and unoriented polymethyl methacrylate on temperature.

A very important and distinctive feature of this material was its behavior during impact testing. During such tests, oriented polymethyl methacrylate underwent local failure over a broad range of test temperatures from −60° up, while the unoriented material under similar conditions underwent total failure.

This behavior of the oriented polymethyl methacrylate during impact testing, when the material is predominantly subjected to compression, may be explained by the fact that at high degrees of orientation, t_{br} under compression, in contrast to t_{br} under tension, is shifted down to −80°.

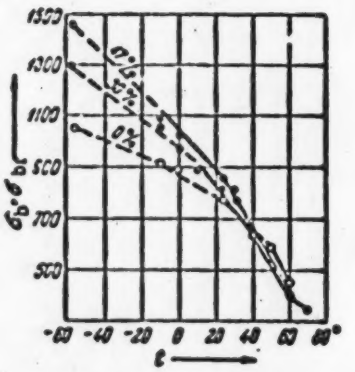

Fig. 4. Dependence of brittle strength (broken line) and of impact elastic limit on temperature; figures on the curves indicate the degree of orientation.

Consideration of results. The possibility of carrying our orientation processes on linear polymers is dependent on a high flexibility of the polymer chains. According to contemporary concepts, the extended form of the macromolecule is the least probable (owing to a tendency to coil into a ball as a consequence of thermal motion). However, owing to limitations imposed by the constancy of the valence angles between C−C bonds, the coiled ball-like form of the molecule is an ideal form which real molecules never attain. With the transition of the polymer from a glass to a highly elastic state, the thermal effect weakens, to a considerable extent, the forces of intermolecular action and thereby facilitates orientational rearrangement. It was found that not only polymer structure, nature, and degree of drawing, but also the temperature-time conditions of the drawing process has a specific effect on the properties of oriented polymers in the glass state. Using experimental material on the orientation of polymers, a number of investigators have established certain basic rules for this process, which aid in analyzing phenomena associated with orientation of macromolecules of linear polymers, including such phenomena as strengthening of the polymer. It is well known that the

strength of linear polymers is dependent chiefly on forces of intermolecular cohesion as well as on cohesive forces of the units of the macromolecules due to the primary chemical valencies.

With an increase in the degree of orientation of the polymer, in the overall balance of forces providing polymer strength, the role of primary chemical valence forces increases, and the role of interparticle cohesive forces decreases. This is connected with the fact that in the orientation process, the individual parts of the chain of the macromolecule are stretched out and oriented in the direction of the applied force, increasing the degree of molecular order in the material (as determined, for example, by birefringence).

A higher degree of molecular order in polymers leads to a more rapid occurrence of relaxation processes; consequences of this are; for example, a slow growth of cracks owing to rapid relief of overloading stress at the ends of the cracks, and also a low susceptibility to high load concentration.

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DIPOLE MOMENTS AND STRUCTURE OF SOME DERIVATIVES OF PERINAPHTHINDENONE

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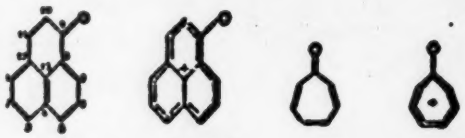
(Presented by Academician A. I. Oparin, May 21, 1959)

Perinaphthindenone (I) and benzanthrone (IV), in which the usual ketonic properties are either very weakly expressed or are entirely absent [1, 2], form very stable complex compounds with protonic and aprotonic acids [2-4], which indicates that there is considerable polarization of the C=O bond. The instability of perinaphthindene and benzanthrene hydrocarbons is apparent in their tendency to go into the oxidized state, which is the stable state for them. The possibility of the existence of the perinaphthindenylium cation, recently obtained by Petit [5] in the form of a complex salt, was proposed by Boekelheide and Holdmann [6], who made an unsuccessful attempt to prepare it.

Molecular orbital calculations of the bond energies of the perinaphthindene system have shown that the energetically most favorable state is a cationoid state with an ensemble of 12 π electrons, which gives the system an aromatic character [7].

Considering these facts, it is possible, following Boekelheide [8], to assume an intraionic character for the $\overset{+}{C}-\overset{-}{O}$ bond in carbonyl compounds of the perinaphthindene series with localization of the negative charge on the oxygen and distribution of the positive charge over the entire carbon syste.



(I) (Ia) (II) (IIa)

The close analogy between the properties of tropone (II) and perinaphthindenone leads one to deduce a perinaphthindenylium oxide structure (Ia) for the latter compound by analogy to tropylium oxide (IIa) and to predict a considerable dipole moment, of the order of 4 D, for the compound, since tropone has a dipole moment in the range of 4.17-4.30 D [9].

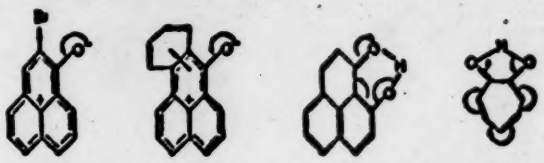
In order to resolve this question, we determined the dipole moments of perinaphthindenone and some of its derivatives.

The dipole moment measurements were carried out by the resonance method in conjunction with the substitution method. The achievement of resonance in the system was determined with high precision by the beat method using a 6E5 indicator tube. The measurements were carried out at a frequency of $5 \cdot 10^6$ cps. The solution in the measuring condenser was isolated from the surrounding atmosphere and was maintained at constant temperature with a precision of $\pm 0.1°$ by means of a water jacket. Refractive indices were determined with an Abbe refractometer with an attachment for maintaining constant temperature. Densities were determined pycnometrically. The molar polarization at infinite dilution was calculated by the extrapolation equation of Hedestrand [10] for perinaphthindenone and its derivatives in benzene and dioxane solutions while for perinaphthindenone in anisole,

an equation proposed by one of us [11] was used. The results of the dipole moment determinations are presented in Table 1.

It is apparent from the data presented that the dipole moment of perinaphthindenone is almost independent of the electrophilic nature of the solvent, and in magnitude it corresponds to the perinaphthindenone oxide structure.

Two of us have found [4] that the introduction of a bromine atom into the 10-position of perinaphthindenone decreases its complex-forming activity with respect to weak acidogens as a result of a reduction in the polarity of the C=O bond due to the induction effect of the bromine. The results of the determination of the dipole moments of 10-bromoperinaphthindenone and 3-bromobenzanthrone confirm this. Table 1 shows that the introduction of a bromine into the perinaphthindenone ring decreased the dipole moment in dioxane by 0.72 D, while a similar substitution in benzanthrone reduced the dipole moment by 1.19 D.



(III) (IV) (V) (VI)

It would be expected that the introduction of an additional aromatic ring in the 10,11-positions of the perinaphthindenone molecule would have an effect similar to that of bromine; i.e., the dipole moment of benzanthrone should be lower than that of perinaphthindenone. A comparison of the dipole moments of perinaphthindenone and benzanthrone in benzene and dioxane is a good illustration of this, because the fusion of the benzene

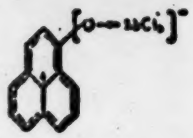
TABLE 1

Compound	Solvent	μ in Debye units
Perinaphthindenone	Benzene	3.89
Same	Dioxane	3.99
"	Anisole	3.98
Benzanthrone	Benzene	3.31
Same	Dioxane	3.37
10-Bromoperinaphthindenone	Dioxane	3.27
7-Bromobenzanthrone	Dioxane	2.18
3-Hydroxyperinaphthindenone	Dioxane	4.28
$C_{13}H_8OSbCl_5$	Dioxane	8.49

ring decreased the dipole moment by 0.5-0.6 D. The introduction of a hydroxyl group into the 7-position of perinaphthindenone makes possible the formation of an intramolecular ring containing a hydrogen bond, thus stabilizing the negative charge of the carbonyl oxygen and removing the C=O group from conjugation with the main skeleton of the molecule as a consequence of intra-ringexchange effects through the hydrogen bridge (V). It is evident that in this case we should expect an increase in the dipole moment over that of perinaphthindenone, and this was confirmed by the measurements.

In contrast, tropolone has a considerably reduced dipole moment as compared to tropone. It is probable that this occurs because of considerable conjugation of the five-membered ring containing a hydrogen bond with the carbon ring, which reduces the overall polarity of the molecule (VI).

The value of the dipole moment of the $C_{13}H_8OSbCl_5$ complex, 8.50 D, makes possible the assumption for this complex of a structure involving a cationoid perinaphthindenylium structure and the transition of the



electronic configuration of the antimony atom to a d^2sp^3 state, by analogy to $HSbCl_6$. The oxygen atom forms a unique bond between the cationoid perinaphthindenylium radical and the antimony atom, acting as one of the addends of the latter and taking part in the coordination sphere with only one of its valencies.

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ON THE SYNTHESIS OF MULTICOMPONENT SOLID SOLUTIONS OF TITANIUM

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(Presented by Academician I. I. Chernyaev, May 15, 1959)

Metallochemistry [1], as one of the offshoots of inorganic chemistry, is the study of the interaction of metals with the elements of the periodic system. Starting with the chemical properties of the elements, it establishes regularities in the formation of metallic solid solutions and compounds. A characteristic feature of the majority of metals is their tendency toward the formation of solid solutions with many elements of the periodic system. This is especially true of metals having an unfilled d-orbital, that is, the transition metals. Titanium is one of these metals. As investigations have shown, it forms solid solutions with many elements [2]. The conditions which determine the formation of solid solutions are a similarity of chemical properties of the crystal lattices and a small difference in the atomic radii.

Titanium forms continuous solid solutions with elements which are analogs of titanium, while with other elements it forms only limited solid solutions.

Starting with the metallochemical properties of elements, in previous papers we considered the question of the solubilities of elements in titanium [2, 3], and we were able to define the basic types of equilibrium diagrams of binary and ternary systems involving titanium [4,5].

Since the rules for the formation of titanium-containing solid solutions have been established, it is now possible to pose and to solve the problem of the synthesis of multicomponent titanium solid solutions having a predetermined composition. This problem can be solved for n-component systems, either for the case in which the interacting elements form continuous solid solutions with titanium or for the case in which limited solid solutions are formed. We have previously demonstrated the possibility of forming multicomponent solid solutions of predetermined composition for the case of nickel solid solutions [6]. 4-, 6-, 15- and 16-Component nickel solid solutions were synthesized in this work. The preliminary calculations of the $\underline{n}$ limiting concentrations of the selected components in nickel solution were completely confirmed, and all of the alloys synthesized were homogeneous nickel solid solutions [6].

On the basis of certain theoretical considerations of metallochemistry, we have calculated the compositions of 5-, 9-, and 10-component titanium solid solutions. The selection of the components and calculation of their limiting concentrations were carried out on the basis of data on the similarities and differences of the chemical properties of these elements with respect to titanium and data on their solubilities in titanium (in the case of limited solubility). The compositions of these alloys were calculated for the following systems:

5 component	Ti — Al — Si — Cr — Fe
9 component	Ti — Al — Sn — Si — V — Nb — Cr — Mo — Cu
10 component	Ti — Zr — Al — Sn — Si — V — Nb — Cr — Mo — Cu

In Table 1 are presented some properties of the elements entering into the composition of these alloys and their calculated limiting concentrations in the 5-, 9-, and 10-component titanium solid solutions synthesized.

TABLE 1

Elements of Titanium Solid Solutions

	5-Component				9-Component								10-Component									
	Al	Si	Cr	Fe	Al	Sn	Si	V	Nb	Cr	Mo	Ca	Zr	Al	Sn	Si	V	Nb	Cr	Mo	Ca	
Difference in atomic radii, in %	4,4	20,0	12,3	13,3	4,4	8,15	20,0	8,2	0,4	12,3	4,4	12,9	8,8	4,4	8,15	20,0	8,2	0,4	12,3	4,4	12,9	
Limiting solubility in α-Ti, wt. %	28,0	0,54	~0,50	~0,50	28,0	22,5	0,54	~2,0	3,0	~0,5	1,0	2,10	100	28,0	22,5	0,54	2,0	3,0	0,5	1,0	2,10	
Calculated composition of the alloy, wt. %	5	0,25	0,25	0,25	5	3,0	0,25	1,0	1,0	0,25	0,5	0,5	5	5	3	0,25	1,0	1,0	0,25	0,5	0,5	

In the present work, solid solutions based on α-solid solutions of titanium with a hexagonal lattice were considered; these were obtained by prolonged annealing, to ensure uniformity, and slow cooling of the alloys to room temperature.

99.8% Ti was used in the preparation of these alloys, while the other elements were of ordinary purity.

Alloys of the compositions presented above, previously calculated on the basis of multicomponent α-solid solutions of titanium, were prepared by fusion of the components in an arc furnace with an inert tungsten electrode. In order to ensure that the case samples would be homogeneous, the samples were reheated three times. The castings were forged to 20-25% compression, and were then given a prolonged annealing under vacuum at 1200-1250° for 10 hours to ensure homogeneity; they were then cooled to 600° and given a prolonged annealing at this temperature for 300 hours.

The alloys were then cooled to room temperature in the furnace, and were subjected to microstructural and x-ray analysis and to microhardness determinations. The microstructural investigations of the 5-, 9-, and 10-component alloys showed that all of these alloys, which were prepared on the basis of the calculations indicated above, were non-equilibrium solid solutions in α-titanium, which were characterized by a peculiar "woven" microstructure, the product of the decomposition of α-solid solution without excess phase (see Fig. 1). We were unable to obtain completely homogeneous polyhedra under this annealing regime.

The x-ray patterns of the annealed alloys were obtained with copper radiation; the patterns of all three alloys contained no lines (within the limits of sensitivity of the method) other than those lines corresponding to the hexagonal lattice of solutions in α-titanium.

The lattice periods of the α-solid solutions, which were measured by a precision method, were the followings

Parameters in A	a	c	c/a
5-component alloy	2,925	4,661	1,594
9-component alloy	2,926	4,677	1,598
10-component alloy	2,932	4,691	1,600

As may be seen from these data, the hexagonal lattice is retained as the composition of the titanium α-solid solutions is increased in complexity. The values of a and c and of the ratio c/a increase with an increase in complexity.

The hardness of these alloys also increased with an increase in the complexity of the systems: 354 kg/sq. mm for the 5-component alloy, 421 kg/sq. mm for the 9-component system, and 492 kg/sq. mm for the 10-component alloy.

Thus, knowing the nature of the interactions of different elements with a given metal and knowing the limiting solubilities of these elements, it is possible to synthesize solid solutions

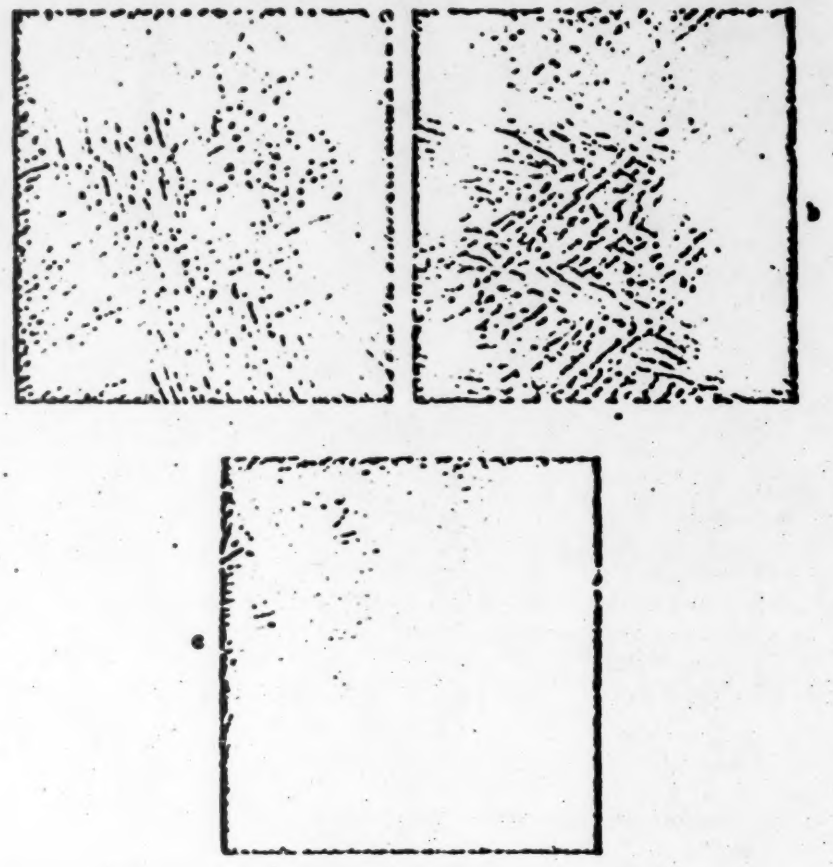

Fig. 1

for which the chemical compositions have been preassigned by means of calculations. The work involved in studying the alloys was done by T. S. Chernova, and the x-ray investigations were carried out by A. Ya. Snetkov.

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THE FORMATION OF DIPHENYLBROMONIUM SALTS BY THE DECOMPOSITION OF $C_6H_5N_2HgBr_3$

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In 1929, one of us found [1, 2] that the decomposition of double salts of benzenediazonium iodide with mercuric iodide could take place by either of two main routes depending on the conditions.

1) $C_6H_5N_2HgI_3 + 2Cu \rightarrow C_6H_5HgI + N_2 + 2CuI$ (under the influence of metals);
2) $C_6H_5N_2HgI_3 \rightarrow [(C_6H_5)_2I]HgI_3$ (unpromoted decomposition).

The first course of the reaction was then extended to the decomposition of double salts of other diazonium halides with the corresponding mercuric halide, and it provided a new method for the synthesis of aromatic organomercury compounds [2].

The second course – unpromoted decomposition – led to the formation (in 10% yield) of the double salt of diphenyliodonium iodide with mercuric iodide. Experiments set up at that time on the unpromoted decomposition of double salts of other diazonium halides with the corresponding mercuric halides remained incomplete (the decomposition, especially in the case of chlorides, requires a long time), and this method, which had promised to be a real method for the preparation of diphenylbromonium and diphenylchloronium salts, has remained unrealized until the present. We are now able to report that the unpromoted decomposition at room temperature of the double salt of benzenediazonium bromide with mercuric bromide (which requires several months standing) proceeds in a manner completely analogous to that of the corresponding iodide compound, and leads to the formation of the double salt of diphenylbromonium bromide with mercuric bromide:

$$4C_6H_5N_2HgBr_3 \rightarrow [(C_6H_5)_2Br]_2HgBr_4 + 4N_2 + 3HgBr_2.$$

On the basis of our previous work on the synthesis of diphenylbromonium salts, it would appear that this reaction proceeds through the preliminary formation of bromobenzene, and this is actually the main course of the reaction. The bromobenzene is then phenylated through the hydrolysis of a new portion of $C_6H_5N_2HgBr_3$, since a similar reaction occurred with $C_6H_5N_2BF_4$ in our previous experiments [3, 4]. This explains the low yield (2.5%) of diphenylbromonium salt. It is obvious that the old, hypothetical explanation of the formation of the diphenyliodonium salt, given by one of us in reference [1] cited above, must be replaced by the new explanation – the primary decomposition product, iodobenzene, is phenylated by means of heterolytic cleavage of the $C_6H_5N_2HgI_3$.

Indeed, when $C_6H_5N_2BF_4$ is decomposed under the usual conditions in a mixture of acetone and iodobenzene, the latter is phenylated and forms (in 7% yield) diphenyliodonium fluoborate. (As we have already reported in reference [3], this reaction does not occur in a medium of pure iodobenzene).

Double salt of diphenylbromonium bromide with mercuric bromide from the diazonium double salt. The double salt of benzenediazonium bromide with mercuric bromide was prepared by adding a solution of mercuric bromide in hydrobromic acid to a solution of benzenediazonium bromide until precipitation was complete. The m. p. of the salt was about 70° (with decomposition).

Found %: C 13.75; 13.77; H 1.00; 1.00
$C_6H_5N_2HgBr_3$. Calculated %: C 13.22; H 0.92

95 g of the resulting double salt of benzenediazonium bromide with mercuric bromide was allowed to decompose unaided at room temperature in a flask fitted with a long air-cooled reflux condenser. Decomposition of the salt was complete after several months (negative test with β-naphthol). The contents of the flask were diluted with ether, and the insoluble precipitate, a mixture of $[(C_6H_5)_2Br]_2HgBr_4$ and $HgBr_2$, was filtered and carefully washed with ether. Steam distillation of the filtrate yielded 23.7 g (87% of theoretical) of bromobenzene with a b. p. of 152-154°. After a second distillation of the material, the b. p. was 153-153.5° (752 mm); $n_D^{21.5}$ 1.5592. The precipitate was reprecipitated with ether from acetone, and 1.07 g (2.5% of theoretical) of the double salt of diphenylbromonium bromide with mercuric bromide was obtained. The salt was washed with a saturated aqueous solution of NaBr, and was then twice reprecipitated from acetone with ether. It had an m. p. of 129-130°, and caused no depression of the melting point when mixed with a known sample*, which had been obtained by adding a solution of mercuric bromide in hydrobromic acid to an aqueous solution of diphenylbromonium fluoborate.

Found %: C 29.02; H 2.17; Br 48.44
$C_{12}H_{10}HgBr_4$. Calculated %: C 29.16; H 2.04; Br 48.51

It is possible that the composition of the salt $([C_6H_5)_2Br]_2HgBr_4$, rather than $[(C_6H_5)_2Br]HgBr_3$) is a consequence of washing it with the sodium bromide solution, which tied up the excess mercuric bromide.

For identification purposes, part of the diphenylbromonium salt isolated from the reaction mixture was converted to diphenylbromonium tetraphenylboron with an m. p. of 163.5-165°. We previously found for $[(C_6H_5)_2Br][(C_6H_5)_4$ an m. p. of 164-165° [3].

Part of the third reaction product – mercuric bromide – was separated from the ether-acetone filtrate after separation of the bromonium salt, and part remained in the distillation flask during the steam distillation. The overall yield was 46.2 g (74%).

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* Found %: C 29.47; 29.47; H 2.05; 2.16; Br 48.36; 48.25; Hg 20.12, 19.92. $C_{12}H_{10}HgBr_4$. Calculated %: C 29.16, H 2.04; Br 48.51; Hg 20.29.

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THE INFRARED SPECTRA AND STRUCTURE OF ORGANOLITHIUM COMPOUNDS OF THE AROMATIC SERIES

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Only a small amount of data is available regarding the structure of aromatic organolithium compounds. In the reviews mentioned in [1], the majority of the authors generally regard these compounds as salt-like, basing this conclusion on their insolubility in hydrocarbons, both aromatic and aliphatic, and on the electrical conductivity of ether solutions of phenyllithium [2]. Ebullioscopic measurements of the molecular weights of phenyllithium and benzyllithium in ether indicate that these organolithium compounds are associated in ether solution (dimers) [2].

With the aim of clarifying the structure of this class of compounds, we obtained the infrared absorption spectra of phenyllithium, o-tolyllithium, p-tolyllithium, mesityllithium, p-biphenyllithium, p-chlorophenyllithium, p-bromophenyllithium, p-iodophenyllithium, α-naphthyllithium, and β-naphthyllithium. These compounds were prepared by the action of solutions of alkyllithium compounds in benzene or hexane on aromatic organoantimony compounds or aryl halides. A comparison of the spectra of aromatic organolithium compounds obtained by the two methods showed that the compounds were identical.

Aromatic organolithium compounds are crystalline materials which are insoluble in hexane and benzene. Therefore, we were forced to use suspensions of the aromatic lithium compounds in vaseline and fluorinated oils in recording the spectra. Moreover, we were able to obtain a weak, but nevertheless sufficiently clear spectrum of the vapor of phenyllithium; an evacuated gas cell, constructed of quartz and fitted with an electric heater and rock salt windows, was used for this purpose. Upon comparing the spectra of the compounds investigated in the present work with the spectra of the corresponding chloro-, bromo-, and iododerivatives taken with the same apparatus, and comparing these spectra with spectra reported in the literature [4], we observed the appearance of several new bands in the spectra of the organolithium compounds; these bands were connected in some manner with C–Li bond (Table 1). Further, on comparing the spectra of vapors (11) and crystals (12) of phenyllithium, it was found that the low-frequency bands (870 and 970 cm^{-1}) disappeared from the spectrum of the phenyllithium vapors, while the band at about 1045 cm^{-1} remained, and its relative intensity increased.

From the data in Table 1 and also from a comparison of the spectra of the aromatic organolithium compounds with the spectra of aliphatic lithium compounds previously reported by us [5], it may be concluded that the band in the 1045-1060 cm^{-1} region is evidently associated with the free C–Li bond or, in any case, with one which takes part in association to only a slight extent, while the lower frequencies can be assigned to C–Li bonds involved in association. It should be noted that both the band at about 1050 cm^{-1} and the lower frequencies as well are close to the vibration frequencies of the C–Li bond in the spectra of aliphatic organolithium compounds.

Thus, the very presence in the spectra of aromatic and aliphatic organolithium compounds of frequencies characteristic of C–Li group vibrations and also the closeness of these frequencies is persuasive indication of the covalent nature of the bond in both classes of compounds. Therefore, in our opinion, the statements in the literature regarding the ionic character of the C–Li bond in aromatic organolithium compounds are incorrect.

Let us consider the data of Table 1 in greater detail. In addition to the intense band at about 1045 cm^{-1}, which we have assigned to the free C–Li bond, the spectra of crystalline phenyllithium also contained intense

bands with frequencies of 875 cm^{-1} and 970 cm^{-1}; these are apparently characteristic vibrational frequencies of C–Li groups taking part in the formation of lithium bonds. In a study of aliphatic organolithium compounds, we established that the major causes of the formation of complexes of organolithium compounds are the formation

TABLE 1

Expt. No.	Compound	Frequency in cm^{-1}			
1	Phenyllithium	875 s	970 s.	–	1043 s
2	o-Tolyllithium	878 s	968 av.	993 s.	1048 s.
3	p-Tolyllithium	880 v. w.	958 w.	993 s.	–
4.	Biphenyllithium	878 v. w.	970 w.	990 s.	1045 s.
5	p-Cl-phenyllithium	–	965 s.	988 v. s.	–
6	p-Br-phenyllithium	883 w.	970 av.	988 s.	1045 av.
7	p-I-phenyllithium	–	970 w.	998 av.	1045 s.
8	Mesityllithium	878 w.	968 w.	985 w.	1052 av.
9	α-Naphthyllithium	879 v. w.	943 s.	–	1059 av.
10	β-Naphthyllithium	880 v. w.	943 s.	–	1054 av.
11	Phenyllithium (vapor)	–	–	–	1045 av.
12	Phenyllithium (cryst.)	–	875 s.	970 s.	1043 s.

of intermolecular lithium bonds and the interaction of dipoles. Moreover, the stability of such complexes depends to a significant extent on the three-dimensional structure of the molecules (steric factor). It is now of interest to trace this dependence into the field of organolithium compounds. In the present work, we investigated the effect on the strength of the lithium bond of not only the purely steric factor, but also the effect of a change in the overall polarity of the molecule by introducing other polar groups or atoms into the organic portion of the molecule.

It is well known that during association of any type, polar groups come into play first, interacting among themselves with the liberation of energy. The hydrocarbon radicals can interfere with complex formation, the extent of the interference depending on the relative location of the various parts of the molecule ("screening"). The screening effect of the remainder of the molecule apart from the lithium appears in the difficulty with which the molecules approach and become oriented for the formation of the lithium bond and also in a decrease in the interaction between dipoles. As a matter of fact, upon comparing the spectra of phenyllithium, p-tolyllithium, o-tolyllithium, biphenyllithium, and mesityllithium, it was found that the extent and type of association of these compounds differed. Thus, intense bands associated with both free and associated C–Li bonds were present in the spectra of phenyllithium and o-tolyllithium, and the frequencies of these bands were in close agreement (except for one new band in the spectrum of o-tolyllithium at about 990 cm^{-1}, which was generally absent from the spectrum of phenyllithium). A comparison of the spectra of these two substances showed that the methyl group in the ortho position had little effect on the degree and nature of the association. This can be explained on the basis that the CH_3 group only insignificantly increases the negative charge on the carbon atom of the C–Li bond, and, consequently, it has little effect on the strength of the lithium bond. Moreover, this effect is weakened by the screening effect of the methyl group, which is located next to the C–Li bond. This same methyl group in the para position (spectrum of p-tolyllithium) changed the spectrum much more significantly. Thus, the band at about 1045 cm^{-1} was not present in the spectrum of p-tolyllithium, while the band at about 990 cm^{-1}, which was already present in the spectrum of o-tolyllithium, became more intense (Fig. 1). The complication introduced by a nonpolar substituent in the para position increases uniformly with the length of the hydrocarbon radical, which leads

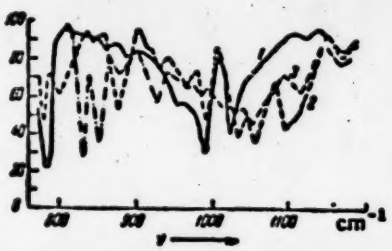

Fig. 1. Infrared absorption spectra of aromatic organolithium compounds: 1) p-tolyllithium, 2) o-tolyllithium, 3) mesityllithium. NaCl prism.

to a decrease in the degree of association (as we have already shown for aliphatic organolithium compounds). Indeed, although there is in the spectrum of p-biphenyllithium a rather intense band at about 980 cm^{-1}, the most intense band is one in the region of 1045 cm^{-1}, which indicates a decrease in the degree of association, although the polarity of this molecule is almost unchanged as compared to the polarity of the other compounds we have been considering.

Finally, the effect of screening is most clearly seen in the spectrum of mesityllithium. In this case, the symmetrically disposed methyl groups strongly inhibit association, and, therefore, the spectrum of mesityllithium shows only the more or less intense band of the free C–Li bond at about 1052 cm^{-1}.

Let us now consider separately the spectra of p-chlorophenyllithium, p-bromophenyllithium, and p-iodophenyllithium (Fig. 2). In contrast to the compounds considered above, each of these three compounds contains two dipoles, C–Li and C–Hal, which, being located para to each other with opposing charges, are cumulative and thereby increase the overall polarity of the molecules. It is evident that this must lead to an increase in the dipole interaction between molecules. Upon comparing the spectra of these three compounds, we found that p-chlorophenyllithium was the most strongly and completely associated, its spectrum showing no absorption in the region of free C–Li group vibration. When the chlorine was replaced by bromine and, further, by iodine, the bands at about 970 and 990 cm^{-1}, which we have assigned to associated C–Li bonds, weakened, and the intensity of the band in the region of 1045 cm^{-1} increased. This is apparently due to a drop in the electronegativity of the halogen atoms in the order Cl > Br > I and to some decrease in the dipole moments of the bonds in the order C–Cl > C–Br > C–I, which leads to a decrease in the effect of the second dipole on the strength of the bond involved in the association. Moreover, the increase in the dimensions of the halogen atoms, which causes additional steric hindrance, must also weaken the association. It must be noted that the total dipole moments of these molecules (calculated taking the moment of the C–Li bond as 1.2 D, and the moments of the C–Cl, C–Br, and C–I bonds as 1.55 D, 1.52 D, and 1.30 D, respectively), although they decrease with replacement of chlorine by bromine and iodine, are still greater (2.5 D) than the dipole moments of such molecules as phenyllithium, p-tolyllithium, etc. In spite of this, the spectra show that the strongly polar molecule p-iodophenyllithium is almost unassociated through lithium bonding, while the slightly polar molecule p-tolyllithium is completely associated. Hence, it must be concluded that the formation of complexes of organolithium compounds and the stability of these complexes is affected by the presence of a second dipole in the molecule, but this effect is not determining, as may be seen from the example presented above.

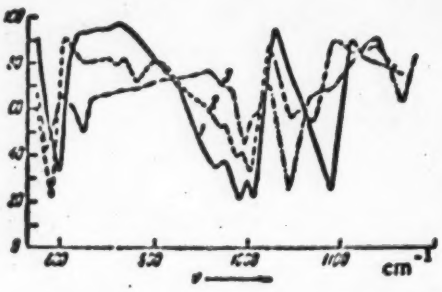

Fig. 2. Infrared spectra of aromatic organolithium compounds: 1) p-chlorophenyllithium, 2) p-bromophenyllithium, 3) p-iodophenyllithium. NaCl prism.

The spectra of α- and β-naphthyllithium differ from the spectra of the aromatic organolithium compounds considered above. In the spectra of these two compounds, the band at about 943 cm^{-1} is the most intense, while the intensity of the band at 1050 cm^{-1} is of low intensity. This is evidently connected with the fact that α- and β-naphthyllithium in the crystalline state are associated.

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ON SOME REGULARITIES IN THE POLYMERIZATION OF PROPYLENE WITH A $TiCl_4$ + AlR_3 CATALYST SYSTEM

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Various points of view regarding the mechanism and regularities of stereospecific polymerization of α-olefins have appeared in the literature [1-4].

Nevertheless, there are many interesting questions regarding the characteristics of stereospecific polymerization. In this connection, it appeared to be of interest to direct attention to some observations made by the present authors during an experimental study of the polymerization of propylene with a catalyst system composed of $TiCl_4$ and $Al(iso\text{-}C_4H_9)_3$. The experiments were carried out in an apparatus similar to that described in a previous paper [5].

The available experimental data provide a basis for the assumption that an exchange reaction takes place between the $TiCl_4$ and the metal alkyl resulting in the formation of an organotitanium compound [6]. Owing to its instability, the latter decomposes the the formation of free radicals. This initiates the polymerization reaction, for example, the polymerization of styrene [7]. Strictly speaking, the organotitanium compound is the catalyst in such a case, and the metal alkyl serves merely as a radical precursor.

The polymerization of propylene is a chain reaction. It was found that only 17 seconds after initiation of the reaction, high molecular-weight polymer is formed, as may be seen from Fig. 1, and the molecular weight remained practically unchanged over a prolonged period (1.5 hours). Thus, the polymer molecule rapidly grows to a limiting size which does not further increase.

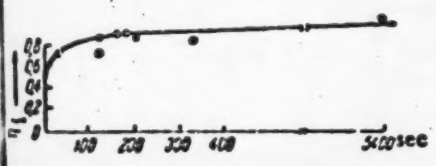


Fig. 1. Change in the intrinsic viscosity of polypropylene with polymerization time.

A continuous decrease in catalyst activity with time was experimentally observed for complex catalysts of the Ziegler type (Fig. 2). It is possible that the drop in activity is connected with a decrease in the amount of organotitanium compound formed with a depression in the alkylation of the titanium chloride.

During polymerization, the rate of absorption of propylene also decreases correspondingly with the decrease in catalytic activity of the complex. In all cases, the propylene absorption curve was obtained under conditions such that the $TiCl_4$ + $Al(iso\text{-}C_4H_9)_3$ catalyst system was formed within a brief time interval, one minute, for example. In this method, the catalyst components practically instantaneously form a highly active catalyst complex, but its activity rapidly decreases with time. The picture was completely different when a change was introduced into the method of catalyst formation. If the $TiCl_4$ was first charged to the reactor and the trialkylaluminum then slowly and uniformly added over a period of, for example, three hours, high catalyst activity was maintained for a prolonged period of time, and the yield of polymer was significantly increased.

In accordance with a proposal by Nenitzescu relative to a radical mechanism for the polymerization, this fact can be explained as follows. In the first method of forming the catalyst, i. e., by the rapid addition of the entire calculated amount of trialkylaluminum to the $TiCl_4$, the formation of a large amount of organotitanium compound and its decomposition with the formation of a large number of radicals occur simultaneously. Since

the reaction is undoubtedly diffusion limited, the majority of the radicals are destroyed by recombination.

When the trialkylaluminum is added gradually, a low concentration of radicals is present at any given instant; therefore, their recombination is difficult. Consequently, catalyst activity is constant, and the yield of polymer increases with an increase in the time of addition of the trialkylaluminum.

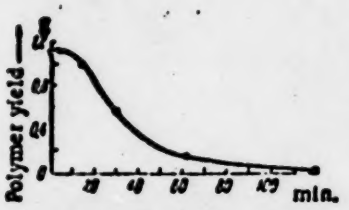


Fig. 2. Decrease in the catalytic activity of the system $AlR_3 + TiCl_4$ with time.

Polymerization processes initiated by Ziegler catalysts are very sensitive to various types of impurities, particularly oxygen, which may be present in the monomer. Therefore, investigators working with Ziegler catalysts have exerted maximum efforts to ensure that the monomer is completely free from even traces of oxygen. However, Fig. 3, shows that the polymer yield is a maximum when the oxygen content of the propylene used in the polymerization is of the order of 0.05 vol. %. When the oxygen content was lower or higher than this value, the yield of polypropylene decreased, and when the oxygen content of the monomer was very high, the catalyst was completely poisoned. This is in agreement with the data of Breslow on the polymerization of ethylene [8]. It is possible that in the presence of oxygen, this catalyst system behaves as a "redox" system. This does not exclude the possibility that the interaction of oxygen with AlR_3 forms alkoxy compounds, which are also active for the practical polymerization of α-olefins.

The effect of reaction temperature on the molecular weight of the polymer was studied at optimum oxygen content of the propylene (Fig. 4). As would be expected, the molecular weight of the polymer decreased with an increase in the reaction temperature from 30 to 80°.

From all appearances, stereospecific polymerization can take place with any of the known initiation mechanisms. It is possible to imagine the occurrence of stereospecific polymerization by either an ionic or a radical mechanism. Stereospecificity of the process is determined by the conditions under which the catalysis is carried out, such as the presence of a solid surface, the effect of highly polar groups, low temperature, etc. —i.e., under conditions such that there is preliminary orientation of the monomer in space, and free rotation of the resulting polymer molecule is limited for the same reasons.

Stereospecific polymerization was discovered during the use of complex catalysts in which the solid phase was formed by $TiCl_3$. Depending on the method by which the latter is obtained, the homogeneity of the catalyst surface varies in degree, and, in accordance with this, catalysts of varying degree of specificity are formed. For example, $TiCl_3$ prepared by reduction of $TiCl_4$ vapors with hydrogen at ~300° has a very homogeneous surface. When such a $TiCl_3$ is used as a component of a catalyst for the polymerization of propylene, up to 95% isotactic polypropylene is obtained [9]. If this same $TiCl_3$ solid phase is formed by reduction of $TiCl_4$ with a trialkylaluminum, as occurs in a Ziegler catalyst, regularity of the $TiCl_3$ crystal lattice is not obtained, since reduction under these conditions proceeds not only to $TiCl_3$, but also to $TiCl_2$ and even to metallic titanium. In accordance with this, the stereospecificity of the Ziegler catalyst is low (the content of isotactic polypropylene is approximately 50%).

Thus, the degree of specificity in this class of catalysts is apparently determined only by the degree of order of the catalyst surface. Therefore, it seems to us that it does not follow that there is a connection between the stereospecificity of the process and the nature of the active centers on the surface, as Natta has reported [10]. We also note that, according to recent reports, it is possible to obtain syndiotactic stereoregular polymers using ordinary radical polymerization initiators in a homogeneous medium [11].

It seems to us that a radical mechanism for polymerization with Ziegler catalysts cannot be excluded, as was first pointed out by Nenitzescu [4].

Titanium trichloride is insoluble in hydrocarbons and forms "sandwich" type crystals; i.e., the titanium ion lies in one plane between two layers of chlorine ions, and it can be found on the surface only at sites where the crystal lattice has been disturbed. Consequently, such a surface is strongly electronegative owing to the octets of the chlorine ions and electrons of the partially reduced titanium, and in an inert solvent the surface is a pseudobase.

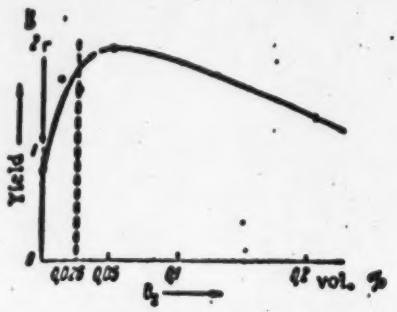
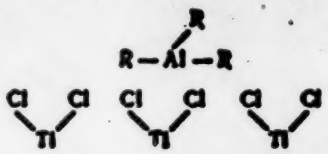


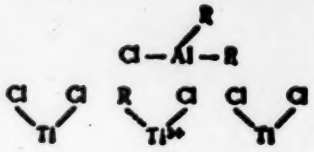
Fig. 3. Effect of oxygen on yield of polypropylene during the polymerization of propylene with $AlR_3 + TiCl_4$.

Fig. 4. Effect of reaction temperature on the intrinsic viscosity of polypropylene.

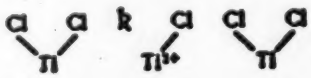
All of the lower aluminum alkyls are dimers (the coordination number of aluminum is four). With an increase in the size of the radical, steric factors decrease the stability of the dimers. $Al(iso\text{-}C_4H_9)_3$ is a monomer. Trialkylaluminum dimers have a weak one-electron bond; therefore, in the presence of the strongly electronegative $TiCl_3$ surface, they dissociate and are adsorbed on the surfaces



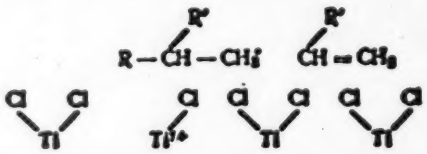
The adsorbed trialkylaluminum enters into an exchange reaction with the $TiCl_3$:



The resulting organotitanium compound decomposes with the formation of a radical, which is adsorbed on the surfaces



Polymerization then takes places



Owing to the presence of a solid surface in the polymerization zone, of all of the possible directions of approach of the monomer to the active center, one will be the most favored (an unusual potential trough), and polymer chain growth will most probably take place in this direction. On the other hand, the presence of the surface prevents the adsorbed molecule from changing its configuration, which leads to a regular structure. Inasmuch as the surface of a Ziegler catalyst is nonhomogeneous (there are vacant sites due to the absence of Cl), this catalyst should not be highly stereospecific in propylene polymerization, as is actually the case.

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VULCANIZING ACTION OF DERIVATIVES OF 2-MERCAPTOBENZOTHIAZOLE

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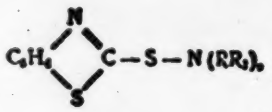
Scientific Research Institute of the Tire Industry

(Presented by Academician A. A. Balandin, May 26, 1959)

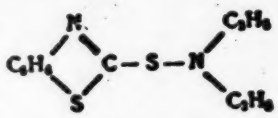
The widespread application in industry of new types of synthetic rubber has required the creation of various different vulcanizing systems having specific actions. The search for such vulcanization systems and in particular, vulcanization accelerators having the desired properties has been made difficult to some extent by the fact that, up to the present time, the question of the effect of the chemical structure of accelerators on their vulcanization activity has not been answered. In this connection, the obtaining of experimental data which would uncover the connection between the chemical structure and the action of vulcanization accelerators is of real theoretical and practical interest.

The object of the work described in the present communication was the investigation of the vulcanizing action of a series of sulfenamide derivatives of 2-mercaptobenzothiazole of different chemical structures; these derivatives had the general formula



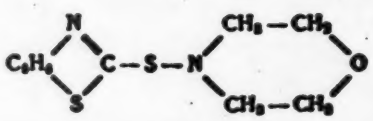
where R and R_1 are alkyl, aryl, azine, and other radicals.

We investigated the following compounds:



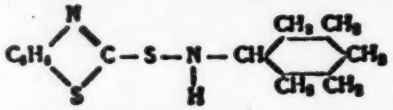
(1)

N,N-diethyl-2-benzothiazolesulfenamide,



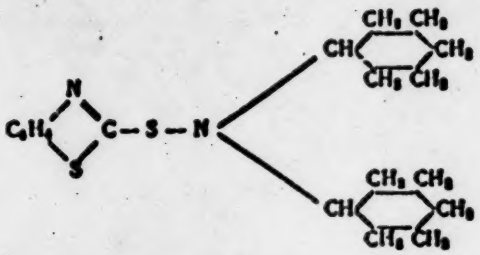
(2)

N-oxydiethylene-2-benzothiazolesulfenamide,



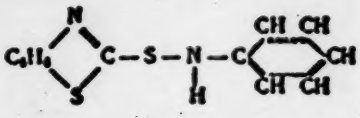
(3)

N-cyclohexyl-2-benzothiazolesulfenamide.



(4)

N,N-dicyclohexyl-2-benzothiazolesulfenamide.



(5)

N-phenyl-2-benzothiazolesulfenamide.

The vulcanization activity of these compounds was evaluated from their action on unreinforced mixtures of butadiene – styrene rubber using kinetic data on the addition of sulfur and the degree of cross-linking – maximum swell – at a vulcanization temperature of 143°. The compounds investigated (as vulcanization accelerators) were introduced in equimolar amounts with respect to 1.0 weight part of N, N-diethyl-2-benzothiazolesulfenamide (sulfenamide BT), which is widely used at the present time as an industrial sulfenamide accelerator.

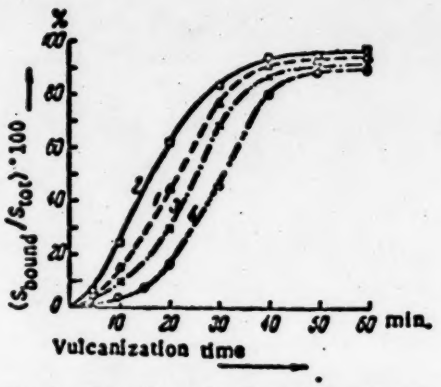
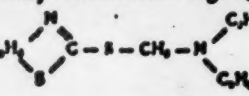
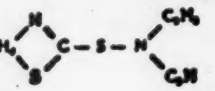
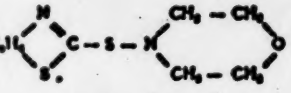
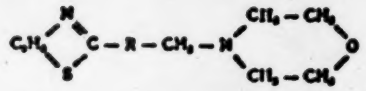


Fig. 1. The effect of sulfenamide derivatives of 2-mercaptobenzothiazole on the kinetics of the addition of sulfur during the vulcanization of unreinforced mixtures of butadiene styrene rubber (SKS-30A): a) N,N-diethyl-2-benzothiazolesulfenamide, 2) N-cyclohexyl-2-benzothiazolesulfenamide, 3) –N-oxydiethylene-2-benzothiazolesulfenamide, 4) N,N-dicyclohexyl-2-benzothiazolesulfenamide.

It was previously established [1, 2] that the kinetics of rubber vulcanization in the presence of sulfenamide derivatives of 2-mercaptobenzothiazole are characterized by the presence of an induction period. The experimental data reported below indicate that the duration of the induction period in vulcanization is determined to a considerable extent by the type of radicals in the amino group.

The data presented in Fig. 1 show that when N-oxydiethylene-2-benzothiazolesulfenamide was used (Curve 3), the induction period of the vulcanization was longer than when N-cyclohexyl- and N,N-diethyl-2-benzothiazolesulfenamide (Curves 1 and 2) were used. A considerable increase in the vulcanization induction period was observed when N-cyclohexyl-2-benzothiazolesulfenamide (Curve 2) was replaced by N-N-cyclohexyl-2-benzothiazolesulfenamide (Curve 4). Curtailment of the vulcanization activity also took place when the cyclohexyl radical was replaced by a phenyl radical.

Thus, the data presented above show that by the introduction of radicals of different structures into the amino group of benzothiazolesulfenamides it is possible to obtain accelerators differing considerably from each other with respect to their vulcanization activity and, in particular, with respect to the length of the vulcanization induction period caused by the accelerator.

Of well-known interest is the hypothesis, established by us, that with a change from sulfenamide compounds with their $-S-N-$ group to compounds containing an $-S-C-N-$ group, there is a sharp acceleration of vulcanization in its initial stage. As may be seen from Fig. 2, the vulcanization rate in the presence of diethylaminomethyl-2-thiobenzothiazole  was considerably higher that when N,N-diethyl-2-benzothiazolesulfenamide,  was used. A similar picture is observed upon comparing the results obtained with N-oxydiethylene-2-benzothiazolesulfenamide,  with those obtained when the corresponding aminomethyl derivative,  was used.

The data presented in Fig. 2 relative to maximum swell show that cross-linking occurs at an earlier stage in the vulcanization process in the presence of aminomethyl derivatives of 2-mercaptobenzothiazole than in the presence of sulfenamide compounds. Thus, for example, a mixture containing N,N-diethyl-2-benzothiazolesulfenamide as a vulcanization accelerator after being heated for 10 minutes at a vulcanization temperature of 143° swelled indefinitely in xylene, while the use of diethylaminomethyl-2-thiobenzothiazole with a 5-minute vulcanization time led to the formation of a cross-linked vulcanizate.

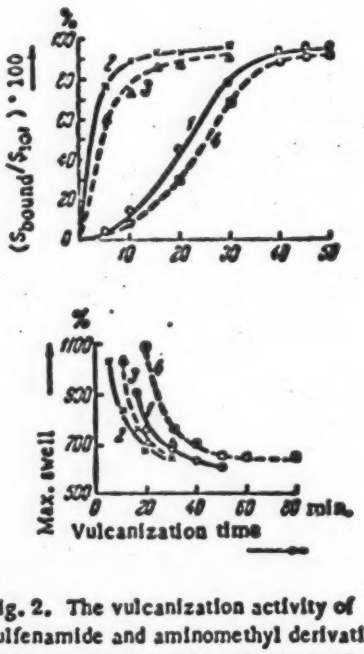


Fig. 2. The vulcanization activity of sulfenamide and aminomethyl derivatives of 2-mercaptobenzothiazole (in unreinforced mixtures of SKS-30A). a) N,N-diethyl-2-benzothiazolesulfenamide, 2) diethylaminomethyl-2-thiobenzothiazole, 3) oxydiethyleneaminomethyl-2-thiobenzothiazole, 4) N-oxydiethylene-2-benzothiazolesulfenamide.

TABLE 1

Exchange Between S^{35}-Labeled Di-2-benzothiazyl Disulfide and Diethylaminomethyl-2-thiobenzothiazole (A) and N-Cyclohexyl-2-benzothiazolesulfenamide (B), %

Vulcanization accelerator	Temperature, °C				
	30	60	80	100	
	time, hours				
	2.5	18	2	2	3
A	13,7	94	98	100	—
B	—	0	~0	00	100

The increased vulcanization activity of aminomethyl derivatives of 2-mercaptobenzothiazole is connected with the greater ease of decomposition of these derivatives into free radicals, as indicated by the data [3] on isotope exchange of aminomethyl and sulfenamide compounds with S^{35} labeled di-2-benzothiazyl disulfide (Table 1). The exchange of benzothiazole radicals between diethylaminomethyl-2-thiobenzothiazole and di-2-benzothiazyl disulfide proceeded at a lower temperature than did exchange in the system N-cyclohexyl-2-benzo-

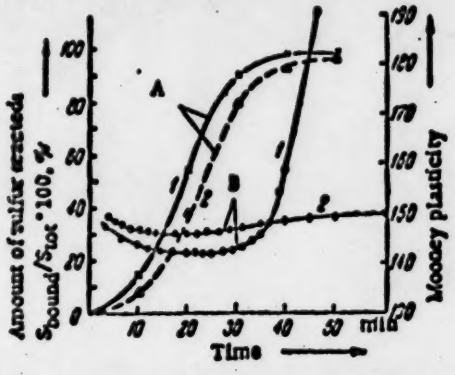


Fig. 3. The action of N,N-diethyl-2-benzothiazolesulfenamide (1) and N-oxydiethylene-2-benzothiazolesulfenamide (2) in SKS-30AM tread recipes containing HAF black. A) kinetics of sulfur addition at a vulcanization temperature of 143°; B) dynamics of the change in Mooney plasticity at 115°.

thiazolesulfenamide – di-2-benzothiazyl disulfide.

The possibility of controlling vulcanization dynamics through the use of appropriate accelerators is technically important.

In recent years, highly disperse furnace blacks have found widespread application in industry, and the presence of these blacks in rubber recipes increases the vulcanization rate and the danger of premature vulcanization (scorch). The use of such recipes of accelerators with a slow action in the initial stage of the process and an increased intensity in subsequent stages makes it possible to obtain the technical optimum of vulcanization and, simultaneously, to eliminate premature vulcanization without an increase in vulcanization time. From this point of view, N-oxydiethylene-2-benzothiazolesulfenamide accelerator has an undoubted advantage over N,N-diethyl-2-benzothiazolesulfenamide with respect both to kinetics of sulfur addition (Fig. 3A) and dynamics of the change in plasticity at a temperature of 115° (Fig. 3 B). These vulcanization kinetics also have a favorable effect on the strength of laminated rubber products [4] and the resistance of vulcanizates to repeated deformation [1].

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**In Russian.

PEPTIDE SYNTHESIS WITH AMINOACYL DERIVATIVES OF NUCLEOSIDES

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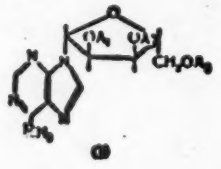
(Presented by Academician A. N. Nesmeyanov, May 22, 1959)

In spite of their important role in the biosynthesis of albumin [1], compounds of nucleotides and ribonucleic acid (RNA) with amino acids have been studied only in the case of aminoacyladenylates [2]. There is no information on other types of amino acid derivatives of nucleotides and RNA, the structure of which has been determined.

In the present work, several O- and N-aminoacyl derivatives of nucleosides were synthesized and studied; these compounds can be considered as models of amino acid derivatives of nucleotides and RNA which are formed as intermediate products in the biosynthesis of albumin. Primarily, we attempted to determine the ability of such compounds to enter into peptide synthesis, i. e., their ability to aminoacylate free amino groups of amino acids or peptides. Two types of aminoacylnucleosides were studied: O-carbobenzoxyphenylalanine* derivatives of adenosine (Type I) and N6-aminoacyl derivatives of cytidine (Type II).

The compounds of Type I were prepared by aminoacylation of free adenosine or 2', 3'-isopropylidenadenosine with cbz-phenylalanine in the presence of dicyclohexylcarbodiimide (pyridine; 20°). It should be noted that under these conditions, only two of the hydroxyl groups in adenosine were acylated, and 2'(3'),5'-di-O-cbz-phenylalanyladenosine (Ia) was apparently formed. When 2':3'-isopropylidenadenosine was acylated, its 5'-cbz-phenylalanyl derivative was formed. The compounds of Type II were also prepared by the carbodiimide method from cytidine and cbz-amino acids using a method described previously [3].

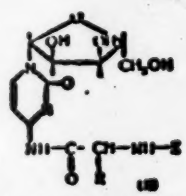
The study of the aminoacylating ability of the O- and N-aminoacylnucleosides synthesized (Types I and II) was carried out under conditions close to natural conditions: in the presence of an enzyme (chymotrypsin)**, at room temperature, and at a pH of 8 (phosphate buffer solution). It was found that under these conditions, both O-(I)- and N-(II)-aminoacylnucleosides readily react with the free amino group of glycine with the formation of a new peptide bond. (See Scheme 2).



(I)

Ia $A_1(A_2) = A_2 = CO-CH(CH_2-C_6H_5)-NH-cbz$; $A_2(A_1) = H$

Ib $A_1 + A_2 = (CH_3)_2C$; $A_3 = CO-CH(CH_2-C_6H_5)-NH-cbz$



(II)

IIa R = $CH_2C_6H_5$; X = H

IIb R = $CH_2C_6H_5$; X = cbz

IIc R = C_6H_5; X = cbz

IId R = $CH_2C_6H_5$; X = $CO-CH(CH_3-CH-CH_3)-NH-cbz$

In Table 1 is presented a list of the peptides which were formed by the action of O- and N-aminoacylnucleosides on the ethyl ester of glycine.

* Carbobenzoxy will hereafter be indicated by cbz.

** It is well known that chymotrypsin is an enzyme which not only hydrolyzes the peptide bond, but also synthesizes it [4].

TABLE 1

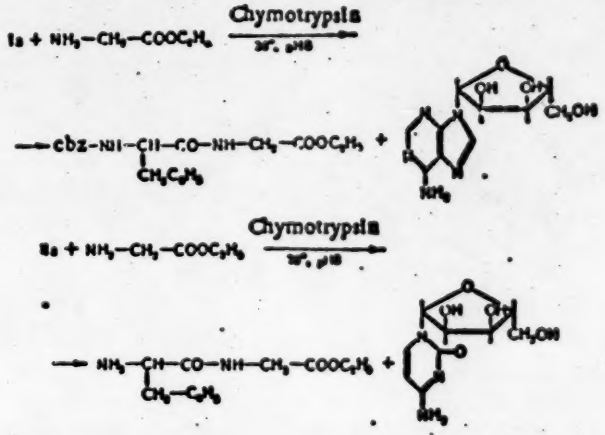
Enzyme Synthesis of Peptides from O-(I)- and N-(II)-Aminoacylnucleosides and the Ethyl Ester of Glycine

Aminoacylating agent	Resulting ethyl esters of the peptides	R_f	Amino acids formed by hydrolysis of the peptides	R_f
I b	Phenylalanylglycine	0.73	Phenylalanine	0.50
			Glycine	0.18
II a	Phenylalanylglycine	0.73	Phenylalanine	0.50
			Glycine	0.18
II b	Phenylalanylglycine	0.73	Phenylalanine	0.50
			Glycine	0.18
II c	Leucylglycine	0.76	Leucine	0.59
			Glycine	0.18
II d	Valylphenylalanylglycine	0.65	Valine	0.42
			Phenylalanine	0.50
			Glycine	0.18

Under these same conditions but in the absence of the enzyme, peptide synthesis was not observed. Only in one case – during the reaction of IIa with the ethyl ester of glycine – were traces of phenylalanylglycine formed in the absence of chymotrypsin. The formation of peptides from I, II, and the ethyl ester of glycine did occur, but under more vigorous conditions (by refluxing in benzene).

The structures of the peptides formed as a result of these reactions were established by means of paper chromatography (for the cbz-peptides, after removal of the cbz group) and by hydrolysis to the amino acids. The succession of the amino acids in the peptides was determined by the dinitrophenyl method.

The data presented above indicate the high reactivity of O- and N-aminoacyl derivatives of nucleosides, which, in turn, indicates the possible participation of compounds of this type in the synthesis of peptide bonds.



EXPERIMENTAL

1. Synthesis of O-aminoacyl derivatives of adenosine. 2'(3'),5'-di-O-cbz-phenylalanyladenosine (Ia). A solution of 0.8 g (0.001 mole) of adenosine and 2.7 g (0.003 mole) of cbz-phenylalanine in 10 ml of absolute pyridine was evaporated almost to dryness; 5 ml of absolute pyridine was added, followed by 1.9 g (0.003 mole) of dicyclohexylcarbodiimide, which was added with stirring. The solution was allowed to stand for 24 hours, and the precipitate was filtered (1.8 g). The solution was evaporated to dryness under vacuum with the addition of alcohol and benzene. The oil was dissolved in chloroform, washed with 10% CH_3COOH, a saturated solution of $NaHCO_3$, and water, and dried over $MgSO_4$.

The chloroform solution was evaporated to 2 ml, and poured into petroleum ether. The precipitate was filtered, allowed to stand overnight under ether, and recrystallized from CCl_4.

The yield of compound Ia was 70%. Decomposition temperature, 88-92°. U. V. absorption in 95% C_2H_5OH: λ_{max} 257-260 mμ (ε 2290). R_f = 0.87 in butanol saturated with water (System 1).

	Found %:	C 63,01; 63,43;	H 5,38; 5,32;	N 11,60; 11,67
$C_{46}H_{43}O_{10}N_5$	Calculated %:	C 63,70;	H 5,20;	N 11,82

5'-O-cbz-phenylalanyl-2',3'-isopropylidenadenosine (Ib). This compound was prepared from 2',3'-isopropylidenadenosine and cbz-phenylalanine in a manner similar to that described above. It was purified by reprecipitation from $CHCl_3$ with petroleum ether. The yield was 55%. Decomposition temperature, 75-80%. U. V. absorption in 95% alcohol: λ_{max} 257-260 mμ (ε 1620). R_f = 0.90 (System 1).

	Found %:	N 14,80; 14,69
$C_{30}O_{33}H_3N_8$	Calculated %:	N 14,47

II. Enzyme synthesis of peptides from O-(I)- and N-(II)-aminoacylnucleosides. To a solution of 100 mg of the hydrochloride of the ethyl ester of glycine in 0.5 ml of water were added 0.3 ml of 2 N NaOH (to a pH of 8-8.1), 2 ml of phosphate buffer solution (pH 8-8.05), 5 mg of crystalline chymotrypsin, and 55 mg of Ia in 2 ml of alcohol. To the suspension were added another 7 ml of buffer solution and, after 10-15 minutes, 4 mg of chymotrypsin. The suspension was agitated for 2 hours and diluted to 50 ml with water; the precipitate was filtered, washed with water, dried, and, for removal of the cbz group, allowed to stand for 1 hour in glacial CH_3COOH saturated with HBr. Absolute ether was added to the solution, and the oil was separated; by means of paper chromotography using a mobile phase consisting of N-C_4H_9OH – H_2O – CH_3COOH (4:5:1) (System 2), the ethyl ester of phenylalanylglycine (~7 mg, R_f = 0.73)* was isolated. Adenosine was detected in the filtrate remaining after separation of the precipitate from the reaction mixture; chromatography gave an R_f of 0.27 and 0.55 in System 1 and in iso-$C_5H_{11}OH$ – Na_2HPO_4 [5] (System 3), respectively. In order to establish the structure of this dipeptide ester, part of it was allowed to stand with 1 N NaOH (1 hour) and then refluxed with 6 N HCl for 12 hours. The hydrolyzate was evaporated to dryness under vacuum with the addition of ethyl alcohol, and the residue was dissolved in water and neutralized. Chromatography in System 2 showed the presence of glycine (R_f = 0.17) and phenylalanine (R_f = 0.50). The succession of the amino acids in the dipeptide was determined by dinitrophenylation of the dipeptide and subsequent hydrolysis [6]. 2 drops of 2,4-dinitrofluorobenzene was added to a solution of the dipeptide ester (5 mg) in 1.5 ml of 20% Na_2CO_3. The mixture was agitated at 40° for an hour. 1 ml of 2 N NaOH was added to the solution, and, after an hour, the solution was extracted with ether. The aqueous layer was acidified and extracted with ethyl acetate. The ethyl acetate was evaporated, 5 ml of 6 N HCl was added, and the solution was refluxed for 10 hours. The hydrolyzate was evaporated to dryness under vacuum, and the residue was dissolved in alcohol and chromatographed in butanol–saturated NH_3. The yellow spot of DNP-phenylalanine was observed (R_f = 0.79, λ_{max} = 360 mμ), which is in agreement with the control sample of DNP-phenylalanine. When the chromatogram was sprayed with ninhydrin, glycine (R_f = 0.33) was detected in the hydrolyzate.

In an experiment carried out under the same conditions but without the chymotrypsin, no dipeptide was found.

In Table 1 are presented the R_f values in System 2 for the ethyl esters of the peptides (after removal of the cbz group from the cbz-peptides) obtained by the method described above using enzyme synthesis with Type I or II compounds and the ethyl ester of glycine. The structures of the peptides were established both by their R_f values (comparison with reference compounds) and by hydrolysis to the amino acids. The formation of peptides was not observed when the reaction was carried out without chymotrypsin**.

* The phenylalanylglycine used as a reference also had R_f = 0.73.

** An exception was IIa, which reacted with the ethyl ester of glycine in the absence of chymotrypsin to form traces of phenylalanylglycine.

III. Reaction of O-(I)- and N-(II)-aminoacylnucleosides with the ethyl ester of glycine in benzene (80°). 40 mg of compound IIa and 200 mg of the ethyl ester of glycine in 5 ml of absolute benzene were refluxed for 5 hours. The reaction mixture was evaporated to dryness under vacuum, and the residue was dissolved in alcohol and chromatographed in System 2.

The chromatogram showed the presence of the ester of phenylalanylglycine (R_f = 0.73). Chromatographing of the reaction mixture in System 3 demonstrated the presence of cytidine (R_f = 0.75).

The reactions of compounds Ia and IIb with the glycine ester proceeded similarly. The reaction resulted in the formation of the ethyl ester of cbz-phenylalanylglycine, and this, after the removal of the benzene, was treated with glacial CH_3COOH saturated with HBr (1 hour, 20°). Absolute ether was added to the solution, and the resulting oil was separated and chromatographed in System 2. The ester of phenylalanylglycine was detected (R_f = 0.73). The structure of the dipeptide was established in a manner similar to that described above.

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A STUDY OF ROUTES FOR THE SYNTHESIS OF RING A OF TETRACYCLINES – A METHOD OF INTRODUCING AN N,N-DIMETHYLGLYCINE RADICAL INTO A CYCLOHEXANE RING

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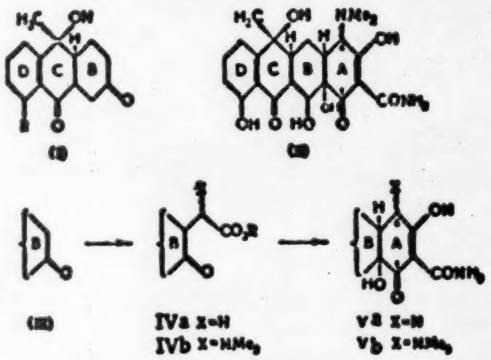
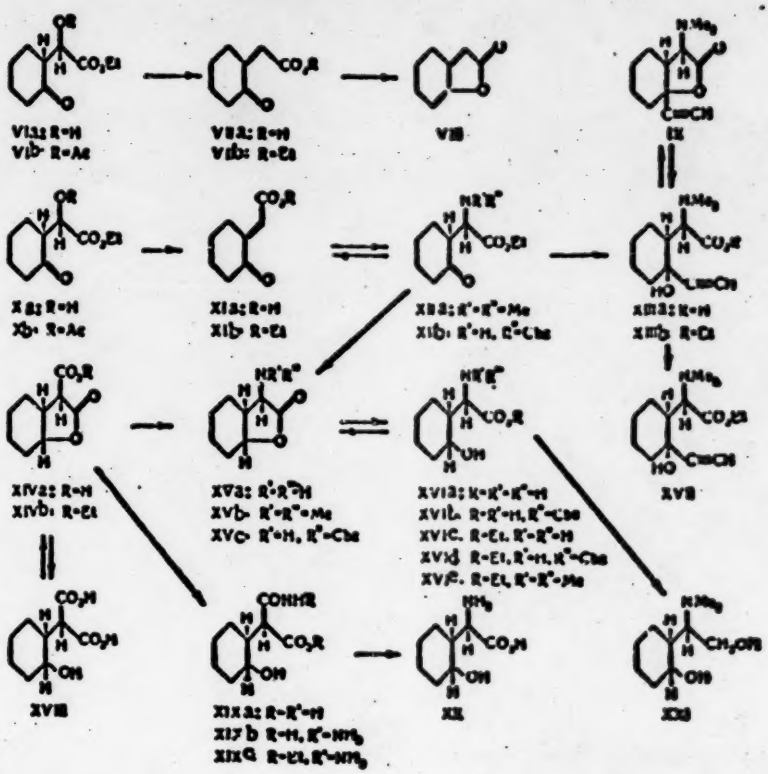
We have previously described tricyclic hydroxy ketones of the type of (I), which are similar to natural tetracycline (II) with respect to the structure of rings C and D and also as to the configuration of the two asymmetric centers [1]. At the same time, with the aim of further investigating these hydroxy diketones for the synthesis of tetracyclines, we developed a general method for the conversion of cyclohexanones (III) through the keto ester (IVa) to compound (Va), which possesses the characteristic hydroxydiketocarboxamide structure of ring A of tetracyclines [2]. In order to use a similar route for the construction of ring A itself, which has an Me_2N group in the 4 position (Vb), it was first necessary to develop a method for the introduction of an N,N-dimethylglycine radical into the cyclohexane ring (III) and to study the reactivity of dimethylaminoketo esters of the type of (IVb). The present communication is devoted to this problem, and it describes a model synthesis and some conversions of the simplest compound of the type of (IVb) – an ester of threo-2-ketocyclohexyl-N,N-dimethylglycine (XIIa).



The introduction of an N,N-dimethylglycine radical into a cyclohexane ring was accomplished under the same conditions and by the same methods as can be used in the case of tricyclic hydroxy diketones (I). For this purpose, cyclohexanone was condensed with the glyoxyl ester or its semiacetate in the presence of pyridine at 100°, and the resulting mixture of stereoisomeric hydroxyketo esters (VIa) and (Xa) (85% yield) was converted to a mixture of unsaturated keto esters (VIIb) and (XIb) (85% yield) by acetylation (AcCl + Py) and deacetoxylation (EtN_3 at 100°). When the resulting mixture of (VIIb) and (XIb) was reacted with dimethylamine in hexane solution at 0°, one of the unsaturated esters added $NHMe_2$, giving an almost quantitative yield of the ester of threo-N,N-dimethylglycine (XIIa), while the other stereoisomer remained unchanged. This less reactive ester was the

cis-isomer (VIIb), since it was hydrolyzed by HCl + AcOH to acid (VIIa) (λ_{max}^{EtOH} 233 mμ, log ε 3.97), which formed the unsaturated lactone (VIII) (λ_{max}^{EtOH} 274 mμ, log ε 4.16) when refluxed with Ac_2O. The more reactive unsaturated ester is the trans-isomer (XIb) (it can be regenerated in 90% yield from the dimethylaminoketo ester (XIIa) by pyrolysis of its oxalate at 135°/0.55 mm); on saponification, it gave the acid (XIa) (λ_{max}^{EtOH} 239 mμ, log ε 3.92), which dimerized and dehydrated to a compound $C_{18}H_{18}O_5$ (XXII) when heated with Ac_2O, but did not form the lactone (VIII). On the basis of these data and considering the transformation (XIb) ⇄ (XIIa) as a reversible process of trans addition of $NHMe_2$, we ascribed to this dimethylaminoketo ester the threo configuration, and this was confirmed as follows.

Alkaline saponification of the previously described [3] lactone of cyclohexanol-2-carbethoxyacetic acid gave trans-2-hydroxycyclohexylmalonic acid (cf. [4]), which in 1 N H_2SO_4 at 20° was gradually lactonized to the corresponding lactone acid; the latter, in view of the reversibility of the lactonization process under the indicated conditions, undoubtedly has the thermodynamically most favored completely transoid configuration (XIVa)*. The stereochemical inequality of the free and lactonized carboxyls in this lactone acid permitted us



to carry out the directed synthesis of threo- and erythro-trans-2-hydroxycyclohexylglycines and their derivatives (by replacement of the first or second of the carboxyls by an amino group). Thus, by the action on acid (XIVa) of $SOCl_2$ (at 45°) and then NaN_3 (in 25% Me_2CO at 0°) with subsequent Curtius rearrangement (0.5 hour at 55°, 1 hour at 80°) and interaction with $PhCH_2OH$, we obtained the cbz derivative (XVc); hydrogenolysis of this compound (Pd/C; 20°, 1 atm.) and hydrolysis (HCl + AcOH; 100°) led aminolactone (XVa); saponification of this with $Ba(OH)_2$ gave the threo-aminohydroxy acid (XVIa), which was easily converted to the original lactone by the action of dilute acids. On the other hand, by amidation (30% NH_3; 20°) and Hofmann rearrangement (0.5 N NaOCl; 40°, lactone acid (XIVa) was converted through acid amide (XIXa) to erythro-aminohydroxy acid (XX).

* The original lactone ester must also have the trans-trans configuration (XIVb), since it can be converted through the hydrazino ester (XIXc) into the same hydrazino acid (XIXb) which is formed by the action of hydrazine hydrate on lactone acid (XIVa).

which was found to be incapable of lactonization, even when evaporated with concentrated HCl. Further conversion from the threo-hydroxy compound (XVI) to keto esters of the type of (XII) was successfully and easily carried out with cbz-aminohydroxy acid (XVIb), which was converted through the Ag salt to hydroxy ester (XVId) to the cbz-aminoketo ester (XIIb) by oxidation of the hydroxy ester with CrO_3 in AcOH. However, we were not able to obtain the corresponding dimethylaminoketo ester by an analogous route (XVId → XVIe → XVIa → XIIa), since by

TABLE 1

Compound	M. p. (decomp.), b. p., n_D^{20}, and solvent for crystallization	Found, %			Calculated, %		
		C	H	N	C	H	N
VIa + Xa	109–109°/0.03 mm; 1.4750	59.95	7.89		59.80	8.05	
	Semicarbazones 233–234° (EtOH)	51.22	7.42	16.63	51.35	7.44	16.98
	Semicarbazones 165–166° (EtOH)	51.53	7.74	16.56	51.35	7.44	16.98
VIb + Xb	115–120°/0.02 mm; 1.4673	59.29	7.79		59.48	7.69	
	Semicarbazones 167–168° (EtOH)	52.34	7.21	16.11	52.16	7.07	16.68
VIIa	104–104° (C_6H_6)	62.95	6.66		62.53	6.54	
	Semicarbazones 197–198° (EtOH)	51.59	6.27	19.35	51.17	6.20	19.90
VIIb	82–83°/0.05 mm; 1.4870	64.25	7.02		63.99	7.76	
	Semicarbazones 172–173° (EtOH)	55.11	7.56	17.52	55.21	7.16	17.20
VIII	66–66°/0.03 mm; 1.5430	70.09	6.15		70.57	6.92	
IX	70–71° (C_6H_{14})	69.29	8.35	6.93	69.53	8.22	6.76
	Picrates 234–235° (EtOH)			13.02			12.96
XIa	124–125° (CH_3O)	62.91	6.58		62.30	6.54	
	Semicarbazones 209–210° (EtOH)	51.42	6.35	20.01	51.17	6.19	19.90
XIb	66–67°/0.03 mm; 1.4523	66.69	7.99		65.99	7.76	
	Semicarbazones 175–176° (EtOH)	55.64	7.43	17.79	55.21	7.16	17.20
XIIa	Oxalates 89–90° (Et_2O from EtOH)	53.28	7.36	6.48	52.89	7.59	6.48
	Semicarbazones 175–176° (EtOH)	55.21	8.52	20.00	54.94	8.51	19.20
XIIb	64–65° (C_6H_{14})	65.11	8.96		64.90	8.86	
	Semicarbazones 125–125° (EtOH)	54.66	6.59	16.11	54.65	6.71	16.36
XIIIa	Monohydrates 249–250° (Me_2CO as H_2O)	59.69	8.75	5.93	59.24	8.79	5.76
XIIIb	97–98° (Et_2O)	68.67	9.18	5.14	68.27	9.15	5.63
	Picrates 123–125° (C_6H_6 from EtOH)			11.52			11.48
XIVa	117–118° (C_6H_{14})	58.59	8.68		58.84	8.57	
XVa	Hydrochlorides 227–228° (EtOH)	50.10	7.36	7.23	50.13	7.58	7.31
XVb	62–63° (C_6H_{14})	65.92	9.20	7.19	65.54	9.25	7.65
	Hydrochlorides 254–255° (EtOH)	54.45	8.50	6.55	54.74	8.28	6.38
	Oxalates 167–168° (EtOH)	53.01	6.89	5.15	52.76	7.10	5.13
XVc	116–115° (C_6H_6 + C_6H_{14})	66.63	6.53	5.24	66.62	6.62	6.48
XVIa	243–245° (Me_2CO · H_2O)	55.37	8.02	5.38	55.67	8.23	5.69
	Hydrochlorides 172–173° (Et_2O from EtOH)	45.76	7.69		45.92	7.66	
XVI b	125–126° ($CHCl_3$ + C_6H_6)	62.06	7.09		62.52	6.88	
XVI c	Oxalates 124–125° (EtOH)	49.45	7.03	5.78	49.47	7.27	6.41
XVI d	92–93° (60% EtOH)	64.61	7.75	6.24	64.66	7.51	6.28
XVII	78–81° (C_6H_{14})	64.73	9.23	5.79	65.37	9.15	5.38
	Picrates 134–135° (EtOH)	50.18	5.47		49.79	5.63	
XVIII	121–122° (AcOEt)	53.58	6.01		53.66	6.98	
XIXa	119–120° (EtOH)	53.76	7.55	7.09	53.72	7.51	6.96
XIXb	177–178° (H_2O)	50.05	7.39	13.19	50.00	7.48	12.96
XX	247–250° (Me_2CO from H_2O)	55.74	8.72	5.19	55.67	8.72	5.40
	Hydrochlorides 254–256° (Et_2O from EtOH)	45.70	7.44	6.03	45.82	7.64	6.68
XXI	70–71° (C_6H_{14})	63.35	11.16	7.25	64.13	11.38	7.16
	Oxalates 138–139° (EtOH)			6.98			7.00
XXII	166–167° (EtOH)	66.14	6.13		66.19	6.25	

ductive methylation [5] of threo-aminohydroxy ester (XVIc), even under mild conditions (pH 5; 25°, 1 atm), ere was formed not the threo-dimethylaminohydroxy ester (XVIe), but its lactonization product (XVb). Therere, for proof of the steric structure of dimethylaminoketo ester (XIIa), we used the reverse conversion – reduction of it to threo compounds (XV) – (XVI) by selective reduction of the keto group with $NaBH_4$ in EtOH at 15°. s would be expected, this reaction resulted in the formation of the trans-trans-dimethylaminolactone (XVb)°, nd this also showed that the original compound actually did have the threo configuration (XIIa).

The dimethylaminoketo ester (XIIa) was studied with regard to the possibility of introducing an ethynyl oup into the molecule, a prerequisite to building the "lower" part of ring A of tetracyclines by the method eviously developed [2]. It was found that dimethylaminoketo ester (XIIa) readily reacts with HC≡CNa in quid NH_3 at −50°, forming the acetylenic hydroxy ester in 60% yield; the latter, by analogy to the product of e borohydride reduction of compound (XIIa), probably has the steric structure (XIIIb). This acetylenic hydroxy ter displayed a great tendency toward lactonization to (IX), and in this regard it was similar to threo-transinohydroxy esters (XVI). It was converted by the action of $(AcO)_2Hg$ in EtOH at 20° to the epimeric erythro

n addition to this lactone, there was also isolated a small amount of a glycol which probably had the structure XI).

isomer (XVII)* , which, in distinction to the original compound, had no tendency toward lactonization, and underwent no change even during distillation at above 100°.

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*Cf. the reversible isomerization of tetracyclines to 4-epitetracyclines under the influence of $(AcO)_2Zn$ [6].

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HYDROLYTIC HYDROGENATION OF CELLULOSE

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Polyhydric alcohols (hexitol, pentitol, erythritol, glycerin, and glycols) have found wide application in the production of valuable synthetic materials – synthetic fibers, alkyd resins, detergents, drying oils, and also as plasticizers and as humectants in the paper, cellophane, perfume, textile, and other industries.

The raw material for the production of polyhydric alcohols is non-edible polysaccharide-containing plant material, the store of which is renewed annually, such as waste from the lumbering and woodworking industries, plant waste from agriculture (straw, corn stalks, sunflower husks, cotton pods, etc.), and also reeds (cane).

We proposed a new, general, catalytic method [1, 2] for the production of polyhydric alcohols from polysaccharides; this process, which we have named hydrolytic hydrogenation, permits hydrolysis of polysaccharides and hydrogenation of the resulting monoses to be carried out simultaneously in a single process.

Hydrolytic hydrogenation of polysaccharides is carried out in an acid medium in the presence of a ruthenium catalyst at elevated temperature and under hydrogen pressure, and it consists of two processes occurring in rapid sequence – hydrolysis and hydrogenation:

$$(C_6H_{10}O_5)_n \xrightarrow{H_2O,\ H_2} nC_6H_{14}O_6,$$
$$(C_6H_{10}O_5)_n \xrightarrow{H_2O,\ H_2} nC_6H_{12}O_6.$$

Under the action of the acid and high temperature, the polysaccharides are hydrolyzed to monoses, and the resulting monoses are rapidly hydrogenated in the presence of the hydrogenation catalyst and hydrogen to the corresponding polyhydric alcohols. This combination of acid hydrolysis and catalytic hydrogenation is important, since it opens up a route for the direct production of polyhydric alcohols in almost quantitative yield from such polysaccharides as cellulose.

Up to the present, pentitols and hexitols have been obtained only by hydrogenation of monoses, and hydrolysis of hemicellulose or cellulose must first be carried out to obtain the monoses. However, hydrolysis of cellulose with dilute acids proceeds only at an elevated temperature and prolonged reaction time, as a result of which there is always considerably further decomposition of the monoses formed, and the practical yield of glucose from cellulose is significantly less than theoretical. However, under hydrolytic hydrogenation conditions, owing to the rapid addition of hydrogen to the glucose, the cellulose can be quantitatively converted to sorbitol, which is quite stable under these conditions. Thus, there is practically no monose present in the free state during hydrolytic hydrogenation, and, therefore, there is practically no possibility of its decomposition. The yield of sorbitol in this case will depend on the hydrogenation rate; if the process is so carried out that the hydrogenation rate is greater than the hydrolysis rate, the cellulose can be quantitatively converted to sorbitol.

Until our work, such a combination of these two processes – hydrolysis and hydrogenation of higher saccharides – had not been described in the scientific literature. There is a report in the patent literature [3] of the hydrogenation of starch in the presence of phosphoric acid and Raney nickel with the formation of sorbitol. However, this reaction takes place only initially, because the two catalysts – phosphoric acid and nickel – rapidly react with each other, particularly at elevated temperatures, with the formation of nickel phosphate, which is inactive for the hydrogenation. The activity of Ru for the hydrogenation of mono- and disaccharides in neutral media is reported in reference [4], but hydrogenation of cellulose in acid media is not mentioned.

The method employed in the present investigation was the following. 2-4 g of cellulose – sulfite or cotton – and 40-50 ml of an 0.7% aqueous solution of phosphoric acid were placed in a glass test tube, and the ruthenium catalyst was then added in an amount calculated to give 0.5% Ru based on the hydrogenatable substance. The test tube was then placed in a rotating autoclave (500 ml volume) which was fitted with an electric heater and which sloped at an angle of 65°. A glass-encased thermocouple well was placed inside the test tube. Hydrogen was pressured into the autoclave to a pressure of 50 atm , and the contents of the autoclave were then heated to the required temperature, the autoclave being rotated continuously. Both sulfite and cotton celluloses were subjected to hydrogenation. The sulfite cellulose contained 99% difficultly hydrolyzable polysaccharides (ash- and moisture-free basis), 0.2% ash, and 5.8% moisture. The cotton cellulose or cotton linters, removed from the seeds by mechanical means, contained 98% difficultly hydrolyzable polysaccharides, 0.0% ash, and 4.0% moisture.

The reaction product was a colorless, odorless solution, from which the catalyst was readily separated by settling or filtration in the case of cellulose hydrogenation. Gaseous by-products were not formed in this process. The resulting aqueous solution of reaction products was purified by ion-exchange resins (cationite and anionite), chiefly for the removal of the mineral acid added during the hydrogenation. The purified solution was evaporated under vacuum until water vapor was no longer evolved, and the resulting product usually crystallized on cooling. The product was analyzed for content of reducible substances (monoses) by the method of Bertrand, and was then subjected to qualitative paper chromatographic analysis. The mobile phase used in the chromatographic analysis was a solution of water, butanol, and acetic acid (5:4:1), and the developer was a 5% solution of silver nitrate in ammonia (d = 0.85). When two-dimensional paper chromatography was used, the second solvent was a solution of pyridine, ethyl acetate, and water (1:2:2), and the developer was the same ammoniacal silver solution. The purity and approximate ratio of components of the hydrogenation product were estimated from the size of the spots and the R_f values. At the same time, the product was analyzed for sorbitol content by a colorimetric method [2] for the determination of sorbitol in the presence of sorbitan, since the latter does not form a basic copper complex (sorbitan is discussed further below).

If the two-dimensional chromatographic analysis indicated that the product was pure, the latter was also analyzed for hydroxyl group content by acetylation, and the melting point, molecular weight (cryoscopic method), and elemental composition were also determined. The yield was determined by weighing the reaction product.

Either barium sulfate or charcoal was used as the support for the ruthenium catalyst. However, the charcoal-supported catalyst gave better results with respect to length of operation, and therefore the basic investigation was carried out in the presence of this catalyst (1% Ru based on the charcoal). After preparation, the activity of the catalyst was tested by hydrogenation of glucose. The test was carried out in the presence of 0.1% Ru (based on the glucose) and 1.0% phosphoric acid at 110° and with a hydrogen pressure of 50 atm ; the catalyst was usually considered active if the glucose was completely hydrogenated within 10-15 minutes with the formation of 99-100% sorbitol. The same portion of catalyst was used ten times without regeneration for the hydrogenation of glucose under the indicated conditions. The limiting stage in the hydrolytic hydrogenation process is the hydrolysis stage. This is proved by the fact that, as indicated above, the hydrogenation of monose proceeds more rapidly and under milder conditions than those required for the hydrolysis of cellulose.

In order to determine the optimum conditions for hydrolytic hydrogenation of cellulose, the effect of the concentration and nature of the mineral acid, the amount of catalyst, the temperature, and the pressure on the rate of the process and the yield of polyhydric alcohol was studied. It was found that the optimum conditions for the hydrogenation of sulfite cellulose in the presence of phosphoric acid and ruthenium catalyst are a temperature of 160-165°, a hydrogen pressure of 60-80 atm , and a hydrogenation time of 50-60 minutes. A phosphoric acid concentration of 0.7% was required. At a lower acid concentration (~0.5%), hydrolysis of the cellulose was slow under the conditions of the experiment, which extended the hydrogenation time (by a factor of 2). A higher acid

concentration (~ 1.5%) accelerated the process only insignificantly; therefore, there was no reason to increase the acidity. Below 160°, hydrolysis of the cellulose was very slow under the conditions of the experiment; therefore, there was practically no hydrogenation. A higher temperature (190-200°) led to decomposition of the reaction products, which was easily detectable by the appearance of a yellow color and an odor in the catalyzate. Moreover, at increased temperatures, the presence of an acid can lead to dehydration of the polyhydric alcohols with the formation of anhydro derivatives of the latter.

It was found that the required hydrogen pressure is 60-80 atm ; at a lower pressure (40 atm) and the optimum temperature and acid concentration indicated above, hydrogenation of the cellulose had not occurred even after 2 hours. A higher pressure (120 atm) had no effect on the hydrogenation rate.

As regards the nature of the acid used, phosphoric or hydrochloric acid was necessary for the production of sorbitol from cellulose. Although hydrolytic hydrogenation takes place within 30-40 minutes at 150-155° in the presence of 0.5% sulfuric acid in the solution, up to 25-40 % sorbitan is formed along with the sorbitol. Sorbitol – the monoanhydride of sorbitol – is formed in this case by a third reaction in the series, namely dehydration of the sorbitols

$$CH_2OH-CHOH-CHOH-CHOH-CHOH-CH_2OH \xrightarrow{-H_2O} CH_2-CHOH-CHOH-CHOH-CH-CH_2OH$$
(with an O bridge between the first and last carbon)

As is well known, sulfuric acid is a powerful catalyst for the dehydration of polyhydric alcohols. At a longer time (1 hour), a higher acid concentration (0.8%), or a higher temperature (180°), the hydrogenation process results essentially in the formation only of sorbitan; hence, this process may also be used as a route for the production of anhydrides of polyhydric alcohols.

Under optimum conditions, the yield of sorbitol from the hydrolytic hydrogenation of sulfite cellulose is 92-96% of the original cellulose. This sorbitol had the following constants: m. p. 107° (literature value, 108°).

Found %:	H 39.4; C 7.7
$C_6H_{14}O_6$ Calculated %:	H 39.5; C 7.69

Free hydroxyl groups (in %): found 55.2; calculated 56.1. Molecular weight: found 184, calculated 182. Colorimetric analysis of this product gave 99.5% sorbitol. There were no reducible substances in the reaction product. On the two-dimensional paper chromatogram there was a single spot with an R_f which corresponded with the R_f of sorbitol.

The yield of sorbitol from the hydrogenation of cotton cellulose was 85-90%. This sorbitol also had constants close to theoretical.

Sorbitan was obtained in 90% yield in the presence of sulfuric acid in special experiments ; OH group content (%): found 41.2; calculated for $C_6H_{12}O_5$ 41.5. There was no reducible material present in the sorbitan, and two-dimensional paper chromatography resulted in a single spot with an R_f corresponding to the R_f of sorbitan.

From the point of view of multiplet theory [5], hydrogenation of the monose resulting from the hydrolysis is a doublet reaction with the index

Multiplet theory considers, on the one hand, structural correspondence, and, on the other hand, energy correspondence. A three-dimensional model has been given for the index indicated above (see Figs. 14 and 15 in reference [5]). According to the model, atomic radii have great significance in catalysis. The metals which are hydrogenation catalysts may be arranged in the following series with respect to the smallest atomic radii (R_x) (the radii presented below are taken from the most recent data [6]):

	Fe	Ni	Co	Cu	Ru	Os	Rh	Ir	Pd	Pt
R, A	1,241	1,246	1,253	1,274	1,325	1,337	1,345	1,358	1,376	1,388
Lattice	A2	A1	A1	A1	A3	A3	A1	A1	A1	A1

It is well known that monoses are hydrogenated over Ni, Cu, Pd, and Pt [7]. From the principle of structural correspondence (two atoms of the molecule superimposed on two metal atoms with the retention of the valence angles [5]), one would expect that maximum activity would lie in the R series above. As Beeck has shown [8], such a maximum activity is actually observed, and it occurs at Rh (A1 lattice; R = 1.345 A) for hydrogenation of the C=C bond. The length of the bond in the activated multiplet complex must be intermediate to a single and a double bond. The C-C bond (1.541 A) is longer than the C-O bond (1.43 A) by 0.111 A, and the C = C bond (1.337 A) is almost as much longer, 0.107A, than the C = O bond (1.23 A); the average is 0.109 A. Theoretically, therefore, on the basis of the principle of structural correspondence it would be expected that maximum activity for hydrogenation of a C = O bond would shift to the left in the above series and would occur at a metal with an A1 or A3 lattice with a shortest interatomic distance equal to 2 × 1.345 − 0.109 = 2.581, i. e., R = 2.581/2 = = 1.291 A. As a matter of fact, of the difficultly acid-soluble metals of the above series, the closest to the indicated requirement is Ru (R = 1.325 A). We have found that hydrolytic hydrogenation does proceed over Pd and Pt, but not as well as over Ru, which is also in agreement with the considerations presented above.

The application of the energy equations of the multiplet theory to the hydrogenation of monoses and to the hydrogenolysis of polyhydric alcohols over Ni has been published previously [9].

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A NEW METHOD FOR THE SYNTHESIS OF HOMOLOGS OF TETRAHYDROFURAN

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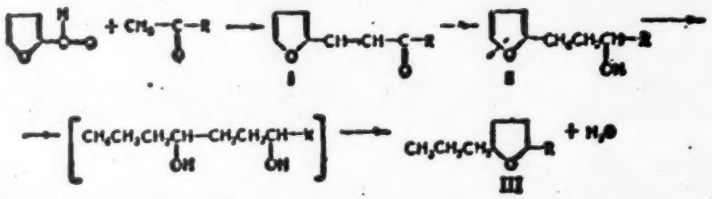
The basic methods for the preparation of tetrahydrofuran and its homologs are the catalytic hydrogenation of furan compounds [1] and cyclization of 1,4-diols [2] or 1,4-halohydrins with the elimination of water or hydrogen halide, respectively. The value of the first of these methods is determined by the availability of the initial furan compounds. The latter can be obtained through utilization of the reactivity of the aldehyde group of furfural or the aromatic properties of the furan ring. The introduction of alkyl or acyl groups into the free alpha position of 2-alkylfurans makes possible the synthesis of a series of 2,5-dialkylfurans. For the preparation of more complex homologs of tetrahydrofuran, it is necessary to start with 1,4-diols of predetermined structure [3].

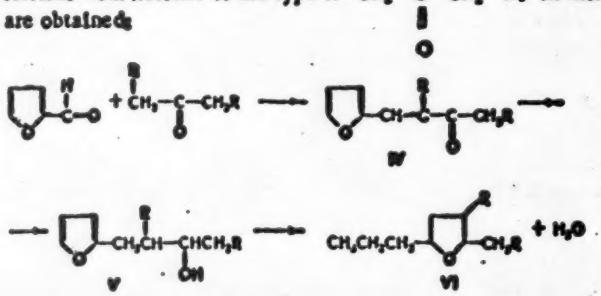
We have developed a new method for the catalytic synthesis of homologs of tetrahydrofuran; this method, which is described in the present paper, consists of the direct conversion of 1-furyl-3-alkanols to tetrahydrofurans of different structures. This method is based on the intermediate formation of 1,4-diols as a result of hydrogenolysis of the furan ring in the 1-furyl-3-alkanol molecule. Under vapor-phase hydrogenation conditions 1,4-diols are readily cyclized with the elimination of water to the corresponding tetrahydrofurans. 1-Furyl-3-alkanols are readily available compounds which may be prepared by hydrogenation of furfurylidene ketones, and these, in turn, are products of the condensation of furfural with aliphatic ketones.

From the point of view of the possibility of synthesizing different homologs of tetrahydrofuran starting with furfural and aliphatic ketones, two cases must be considered.

1. The condensation of furfural with methyl alkyl ketones. In this case, 2-n-propyl-5-alkyltetrahydrofurans (III) are obtained, as may be seen from the following scheme:



2. Condensation of furfural with ketones of the type $R-CH_2-C(=O)-CH_2-R$. In this case, 2-n-propyl-4,5-dialkyltetrahydrofurans (VI) are obtained:



The structure of the di- and trialkyltetrahydrofurans obtained by vapor-phase hydrogenation of 1-furyl-3-alkanols confirms the reaction mechanism given above: hydrogenolysis of the furan ring takes place first, and the resulting 1,4-alkandiol is converted to the corresponding tetrahydrofuran by intramolecular elimination of water. Here we have a peculiar case of the simultaneous hydrogenolysis of a furan ring and closure of a new tetrahydrofuran ring, three of the carbon atoms of which were present in the original compound as a side chain. This circumstance opens up broad possibilities for the synthesis of various tetrahydrofuran homologs, since the structure of the side chain in the 1-furyl-3-alkanol, which determines the structure of the newly formed substituted tetrahydrofuran ring, can be changed by changing the structure both of the carbonyl-containing group in the furan compound and of the aliphatic ketone.

Hydrogenolysis of the furan ring, which is the necessary first stage in the process of converting 1-furyl-3-alkanols to homologs of tetrahydrofuran, proceeds readily in the presence of various catalysts containing Group VIII metals, for example, in the presence of Pt/C, skeletal Ni/Zn, and skeletal Cu/Al catalysts. Platinized carbon was widely used in our experiments. The main side reactions occurring over this catalyst are: a) isomerization of the resulting homologs of tetrahydrofuran to aliphatic ketones [4], b) formation of 1,4-alkandiols, and c) hydrogenation of the 1-furyl-3-alkanols to 1-tetrahydrofuryl-3-alkanols. The first two reactions become quite appreciable at elevated temperatures (above 250°), and the last of these reactions, on the contrary, occurs only at decreased temperatures. The hydrogenation of 1-furyl-3-alkanols at 220-240° usually gives tetrahydrofurans in yields of 50-70%. At 300°, 2-methyl-5-n-propyltetrahydrofuran was formed in 30% yield from 1-furyl-3-butanol.

By condensing furfural with acetone, methyl ethyl ketone, and methyl propyl ketone in the presence of a solution of NaOH, we obtained the corresponding furfurylidene methylalkyl ketones (I) in yields of 70-80%. The condensation of furfural with diethyl ketone was less satisfactory; the yield of the corresponding furfurylidene ketone (IV) was 50-55%.

The hydrogenation of the furfurylidene ketones to 1-furyl-3-alkanols (II, V) was carried out in the liquid phase over skeletal Cu/Al catalyst at 130-140° and resulted in yields of up to 95%. The resulting 1-furyl-3-alkanols had the following properties:

1) 1-Furyl-3-butanol, b. p. 67-69° (4 mm); d_4^{20} 1.0202; n_D^{20} 1.4754.

2) 1-Furyl-3-pentanol, b. p. 77-78° (4 mm); d_4^{20} 1.0023; n_D^{20} 1.4750.

3) 1-Furyl-3-hexanol, b. p. 97-98° (5 mm); d_4^{20} 0.9861; n_D^{20} 1.4707.

4) 1-Furyl-2-methyl-3-pentanol, b. p. 98-100° (2 mm); d_4^{20} 1.0587; n_D^{20} 1.5663.

The vapor phase hydrogenation of the 1-furyl-3-alkanols was carried out at ordinary pressure. The liquid catalyzates, which were obtained in practically quantitative yields, were dried with calcium chloride and then distilled in an efficient column at reduced pressure. The fractions corresponding to the tetrahydrofuran homologs were redistilled at reduced pressure, this time over sodium, from a flask fitted with a dephlegmator. The resulting tetrahydrofurans had the following properties:

1. 2-Methyl-5-n-propyltetrahydrofuran, b. p. 140-142° (755 mm); d_4^{20} 0.8380; n_D^{20} 1.4200. MR_D found, 38.72. Calculated for $C_8H_{16}O$, 38.59.

2. 2-Ethyl-5-n-propyltetrahydrofuran, b. p. 60-61° (22 mm); d_4^{20} 0.8464; n_D^{20} 1.4297. MR_D found 43.38. Calculated for $C_9H_{18}O$, 43.21.

3. 2,5-Di-n-propyltetrahydrofuran, b. p. 54-56° (6 mm); d_4^{20} 0.8390; n_D^{20} 1.4290; MR_D found, 47.98; calculated for $C_{10}H_{20}O$, 47.82.

	Found %	C 77.23; H 12.00
$C_{10}H_{20}O$.	Calculated %	C 76.90; H 12.91

4. 3-Methyl-2-ethyl-5-n-propyltetrahydrofuran, b. p. 67-67.5° (16 mm); d_4^{20} 0.8461; n_D^{20} 1.4312. MR_D found, 47.79. Calculated for $C_{10}H_{20}O$, 47.82.

	Found %	C 77.11; H 12.61
$C_{10}H_{20}O$.	Calculated %	C 76.90; H 12.91

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A NEW METHOD FOR THE PREPARATION OF AROMATIC BISMUTH COMPOUNDS BY OXIDATION OF MIXTURES OF ARYLHYDRAZINES AND BISMUTH TRICHLORIDE WITH ATMOSPHERIC OXYGEN IN THE PRESENCE OF CUPRIC CHLORIDE

A. B. Bruker and K. M. Malkov

(Presented by Academician I. L. Knunyants, June 1, 1959)

Heteroorganic aromatic compounds were first obtained by Fischer and Erhard [1], who started with an arylhydrazine and an inorganic compound of the appropriate element. They obtained diphenylmercury by oxidizing phenylhydrazine in ether solution with mercuric oxide. Seide, Scherlin and Brass [2] prepared phenylmercury acetate in a medium of acetic acid in the presence of copper or its salts. Wieland and Madelung [3] prepared triphenylarsine by oxidizing phenylhydrazine with benzenearsonic and diphenylarsinic acids. Attempts to form aromatic arsenic compounds by oxidation of phenylhydrazine with arsenic acid failed. Seide, Scherlin and Brass [4] obtained a mixture of phenyl- or tolylarsine oxide, diphenyl- or ditolylarsine oxide, and triphenyl- or tritolylarsine by the interaction of phenyl- or tolylhydrazine in aqueous solution with arsenic acid in the presence of copper or its salts. The p-chloro-, p-bromo-, p-fluorophenyl-, and diphenylarsenic compounds [5] were prepared by this method.

Attempts to prepare aromatic aresenic compounds by the oxidation of p-nitrophenylhydrazine with a solution of arsenic acid were not successful.

In the work of Bruker and Maklyaev [6] on the role of copper in the preparation of aromatic organometal compounds by diazo or hydrazino reactions it was shown that if the starting material for the reaction is an inorganic arsenic compound, then the presence of copper or its salts is required for the preparation of aromatic arsenic compounds, while if aromatic arsenic compounds are to be arylated, the reaction will proceed without the presence of any special catalyst.

Attempts to prepare aromatic antimony or bismuth compounds by similar routes gave negative results. This can apparently be explained, on the one hand, by the low solubility of antimony, arylantimony, and bismuth acids in water and organic solvents, and, on the other hand, by the significantly lower oxidizing power of antimony and bismuth acids as compared to arsenic acids.

In previously published communications we have described a new method for the preparation of aromatic heteroorganic compounds involving the interaction of aryl hydrazines with chlorine derivatives of arsenic and antimony in hydrochloric acid solution using atmospheric oxygen as the oxidizing agent in the presence of cupric chloride. Phenyl-, diphenyl-, tolyl-, naphthyl-, and p-fluorophenyl-antimony compounds were prepared by this method [7, 8]. Aromatic antimony compounds were also prepared by the interaction of phenylhydrazine with antimony pentachloride in hydrochloric acid solution in the presence of cupric chloride and atmospheric oxygen [8]. Aromatic arsenic compounds were obtained by oxidation of a mixture of phenylhydrazine and arsenic trichloride with atmospheric oxygen in the presence of cupric chloride [9]. Phenylmercury chloride was prepared by the interaction of phenylhydrazine and mercuric chloride in a hydrochloric acid medium in the presence of cupric chloride [10]. The present paper describes an experiment on the preparation of triphenylbismuth by the interaction of phenylhydrazine hydrochloride with bismuth trichloride in the presence of cupric chloride and atmospheric oxygen.

32 g of bismuth trichloride, 3 g of cupric chloride, and 3 g of ferric chloride were dissolved in dilute hydrochloric acid (45 ml of HCl, d = 1.19, and 600 ml of water) in an open vessel, and 43 g of phenylhydrazine

hydrochloride was gradually added with stirring. The reaction mixture was stirred for 16 hours, and an aqueous solution of ammonia (25%) was then added to an alkaline reaction. The resulting precipitate was suction filtered, dried in air, and extracted with chloroform. The solvent was evaporated from the chloroform extract, and 10 g of a substance with a melting point of 75° was obtained. Recrystallization of this material from methyl alcohol yielded 8 g of triphenylbismuth which melted at 77-78°. The literature value of the melting point is 77° [12].

A mechanism for the formation of aromatic arsenic and antimony compounds by diazo and hydrazino reactions was presented in previously published communications [11]; this mechanism can be represented by the following equations:

$$ArNH-NH_2\cdot HX + O_2 \xrightarrow{CuCl_2} ArN_2X + 2H_2O.$$

$$ArN_2X + MeX_3 \rightarrow ArN_2X\ MeX_3 \xrightarrow[\text{or in the presence of metals}]{\text{in alkaline medium}} ArMeX_4 + N_2.$$

$$ArN_2X + MeX_3 \rightarrow ArN_2X\ MeX_3 \xrightarrow[\text{presence of a reducing agent}]{\text{decomposition in the}} ArMeX_2 + N_2.$$

$$ArN_2X + ArMeX_2 \rightarrow ArN_2X\cdot ArMeX_2 \begin{cases} \xrightarrow{\text{decomposition}} Ar_2MeX_3 + N_2 \\ \xrightarrow[\text{presence of a reducing agent}]{\text{decomposition in the}} Ar_2MeX + N_2. \end{cases}$$

$$ArN_2X + Ar_2MeX \rightarrow ArN_2X\cdot Ar_2MeX \begin{cases} \xrightarrow{\text{decomposition}} Ar_2MeX_3 + N_2. \\ \xrightarrow[\text{presence of a reducing agent}]{\text{decomposition in the}} Ar_3Me + N_2 \end{cases}$$

$$\left[Ar-N\equiv N\right]^+_3 [MeX_4]^- \rightarrow [ArN=N-MeX_3]^+ X^- \rightarrow ArMeX_4 + N_2.$$

I II

The conversion of I to II is catalyzed by the presence of copper (or other metals), which donates one electron to the nitrogen and accepts one from the metal being reacted.

$$Ar-N\equiv N \xrightarrow{Cu} [Ar-N=N-MeX_3]^+X^- \rightarrow ArMeX_4 + N_2.$$

$$MeX_4^-$$

The formation of triphenylbismuth from phenylhydrazine and bismuth trichloride in the presence of atmospheric oxygen and copper has much in common with the mechanism of the formation of aromatic arsenic and antimony compounds. In general, this comes about through the oxidation of the arylhydrazine by atmospheric oxygen to benzenediazonium chloride; the latter interacts with the bismuth trichloride with the formation of a binary compound, which is reduced by the arylhydrazine with the formation of an aromatic bismuth compound. The difference is that the benzenediazonium chloride does not react with bismuth trichloride under these conditions to give a binary compound of the type $ArN_2X\cdot BiX_3$, and therefore, primary or secondary aromatic bismuth compounds are not obtained. The binary compound formed in this case, $(ArN_2X)_3\cdot BiCl_3$, reacts with phenylhydrazine to give triphenylbismuth.

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THE FORMATION OF TROPYLIUM BY THE ACTION OF MONOHALOCARBENES ON BENZENE

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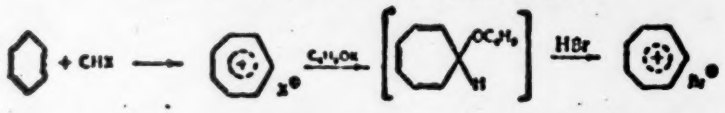
We have recently shown that the action of hydrogen peroxide on tropylium salts proceeds with the elimination of one carbon atom and the formation of benzene [1].

However, the reverse reaction – expansion of the benzene ring with the formation of the tropylium cation – has thus far remained unknown. There are indirect data (deuterium distribution in reaction products) forming a basis for the assumption that in the bombardment of deuterated monoalkylbenzene vapors with electrons in a mass spectrometer, not the benzyl cation but the isomeric tropylium cation is formed [2].

We have been able to show that the action of potassium tert-butylate on CH_2Cl_2, CH_2Br_2, or CH_2I_2 followed by treatment with hydrogen bromide forms, in all of these cases, small amounts of tropylium bromide. This can be explained by the intermediate formation of monohalocarbenes, CHX, and their interaction with benzene according to the schemes

$$CH_2X_2 + C_4H_9OK \rightarrow CHX + C_4H_9OH + KX,$$



Experiments carried out under different conditions showed that the concentration of starting materials and the reaction time have no substantial effect on the yield of tropylium bromide. The yield of tropylium cation increased somewhat with an increase in temperature. As is well known, there has been a considerable amount of work in recent years devoted to the study of the reactions of dihalocarbenes, CX_2, formed by alkaline hydrolysis of haloforms (see review [3]). However, the reaction studied by us is the first case in which the formation of unsubstituted monohalocarbenes has been observed.

While the rate of alcoholysis of methylene halides by an S_N2 mechanism increases in the order $CH_2Cl_2 < CH_2Br_2 < CH_2I_2$ [4], the yield of tropylium salt from benzene increases in the reverse order $CH_2I_2 < CH_2Br_2 < CH_2Cl_2$. This is in agreement with the data of Hine [5] relative to the ease of formation of dihalocarbenes from haloforms.

Thus, on the basis of our data it may be assumed that alcoholysis of methylene halides partly proceeds with the intermediate formation of monohalocarbenes, CHX. The tropylium salt is formed by the addition of the monohalocarbene to the benzene; this is the first example of the direct conversion of benzene to a tropylium salt.

EXPERIMENTAL

The Interaction of Benzene with Methylene Chloride

a) To a boiling mixture of 8.4 g (0.075 mole) of dry potassium tert-butylate (free of tert-butyl alcohol) and 200 ml of absolute benzene was added, with stirring, 19.1 g (0.225 mole) of methylene chloride. Upon the

completion of the addition of the methylene chloride, the mixture was stirred at 60° for 4 hours. On the following day, the thickened, light brown mass was filtered, and the filtrate was evaporated under vacuum; dry hydrogen bromide was then passed into the solution. The resulting precipitate was filtered, washed with absolute benzene, and dried under vacuum. 0.24 g of tropylium bromide was obtained; this corresponds to a yield of 1.9% calculated on the $(CH_3)_3COK$. This substance was dissolved in water, and after treatment with sodium bicarbonate and extraction with benzene, it was again precipitated with hydrogen bromide. Tropylium chloroplatinate was precipitated from aqueous and alcoholic solutions of the bromide by the action of H_2PtCl_6. The infrared and ultraviolet spectra of tropylium bromide were identical with those obtained by Doering and Knox [6].

b) 15.3 g (0.18 mole) of CH_2Cl_2 was added, with stirring and over a period of 30 minutes, to a mixture of 10.7 g (0.095 mole) of potassium tert-butylate and 200 ml of benzene at 20°. The reaction mixture was stirred for 7 days, after which the precipitate was separated, and a stream of dry hydrogen bromide was passed into the filtrate. The resulting precipitate was treated with water, and the aqueous solution was made alkaline with sodium bicarbonate. The resulting ditropyl ether was extracted with benzene. Tropylium bromide separated when HBr was passed into the benzene solution; the yield was 0.16 g or 1.4%.

The Interaction of Benzene with Methylene Bromide

a) Over a period of 1 hour, 26 g (0.15 mole) of CH_2Br_2 was added, with stirring, to a mixture of 11.2 g (0.1 mole) of potassium tert-butylate and 200 ml of benzene at 6°. After the addition of half of the CH_2Br_2, the mixture congealed and was diluted with 200 ml of benzene. At the conclusion of the addition of the CH_2Br_2, the mixture was stirred for 1 hour at 6°, and then for 2 days at room temperature. 0.035 g of tropylium bromide was obtained by the usual treatment; the yield was 0.2%.

b) 0.06 g of tropylium bromide, 0.4% yield, was obtained from 8.9 g (0.08 mole) of potassium tert-butylate, 27.8 g (0.16 mole) of CH_2Br_2, and 200 ml of benzene at room temperature.

c) 0.2 g of tropylium bromide, 1.2% yield, was obtained from 11.2 g (0.1 mole) of $(CH_3)_3COK$, 22.8 g (0.13 mole) of CH_2Br_2, and 200 ml of benzene; the reaction was carried out in boiling benzene.

The Interaction of Benzene with Methylene Iodide

0.015 g of tropylium bromide, 0.1% yield, was obtained from 10.3 g (0.09 mole) of potassium tert-butylate, 44.4 g (0.17 mole) of CH_2I_2, and 200 ml of benzene at room temperature.

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INVESTIGATION OF THE CARBOHYDRATE PART OF C-SUBSTITUTED MONOSES

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(Presented by Academician A. I. Oparin, June 5, 1959)

Up to the present time, the attention of investigators studying carbon-substituted sugars has been centered chiefly on the properties and transformations of the aglucon part of the molecule, and as a result, little attention has been given to the carbohydrate radical. Most of the C-substituted monoses have been obtained in the form of acetylated derivatives as a result of the usual method of synthesis, which includes a final acetylation stage. Deacetylated and methylated products have been obtained in specific instances [1, 2].

In an attempt to fill in this gap, we have undertaken an investigation of the properties of the carbohydrate part of C-substituted monoses. With this aim, we first studied methods for the preparation of pure deacetylated derivatives. Deacetylation by means of dry ammonia in absolute methanol appeared to have the best prospects here. This method was used to prepare 1-phenyl-1-desoxyxylose, 1-p-anisyl-1-desoxyglucose, and 1-phenyl-1-desoxygalactose. These products were used for the preparation of previously unknown benzoylated derivatives by the action of benzoyl chloride in pyridine.

By the replacement of the primary alcohol group in 1-phenyl-1-desoxyglucose, it was possible to prepare the trityl and tosyl derivatives.

1-Phenyl-1-desoxy-d-glucuronic acid, which is more conveniently named 6-phenyl-1-gulonic acid, was synthesized by oxidation of 1-phenyl-1-desoxyglucose with nitric acid. On the basis of the analytical data and also considering the tendency of aldonic acids to form γ-lactones, the following formula may be assigned to this acid

EXPERIMENTAL

1-Phenyl-1-desoxyxylose. 2 g (0.006 mole) of 1-phenyl-1-desoxy-2,3,4-triacetylxylose, prepared by a previously described method [2], was dissolved in 100 ml of absolute methanol. The solution was cooled with ice and saturated with ammonia (the weight increase was 14.6 g), and it was then allowed to stand for a day. The solution was evaporated on a water bath, the dry residue was treated with warm ether for the removal of the acetamide, and the product was recrystallized from methyl acetate. The yield was 0.91 g (73% of theoretical). The 1-phenyl-1-desoxyxylose was obtained in the form of white needles with an m. p. of 148-148.5°. This substance is described here for the first time.

Found %: C 62.77; 62.62; H 6.86; 6.71. $C_{11}H_{14}O_4$. Calculated %: C 62.86; H 6.67.

1-Phenyl-1-desoxy-2,3,4-tribenzoylxylose. 1 g (0.005 mole) of 1-phenyl-1-desoxyxylose, synthesized by the method described above, was dissolved in 10 ml of pyridine, and the solution was heated to 100°. 5 ml (0.04 mole) of benzoyl chloride was then added, and the solution was heated for one hour at a temperature of about 100-105°. The reaction mixture was then cooled, and the excess benzoyl chloride was decomposed by the addition of ice. 100 ml of dichloroethane was then added, and the pyridine was removed by carefully washing the solution with cold water, 3 N sulfuric acid, and then with a cold saturated solution of sodium bicarbonate.

The dichloroethane extract was dried over sodium sulfate, and the solvent was then evaporated under vacuum (water aspirator) at 50° until a thick syrup was formed.

Recrystallization from absolute alcohol gave 1.57 g (63.5% of theoretical) of a colorless, crystalline product with an m. p. of 168°. This substance is described here for the first time.

	Found %:	C 73.23; 73.44;	H 5.10; 5.11
$C_{32}H_{26}O_7$.	Calculated %:	C 73.56;	H 4.98

1-Anisyl-1-desoxyglucose. Deacetylation of 1-p-anisyl-1-desoxy-2,3,4,6-tetraacetylglucose was carried out by the method described above for the similarly substituted xylose. From 2.57 g (0.006 mole) of the starting material was obtained 1.47 g (93% of theoretical) of the deacetylated material, which, after recrystallization from methanol, had an m. p. of 225°. This substance is described here for the first time.

	Found %:	C 57.45; 57.75;	H 6.75; 6.88
$C_{13}H_{18}O_6$.	Calculated %:	C 57.78;	H 6.67

1-Anisyl-1-desoxy-2,3,4,6-tetrabenzoylglucose. The benzoylation of 1-anisyl-1-desoxyglucose was carried out by the method described above, using benzoyl chloride in pyridine. 2.35 g (92.5% of theoretical) of benzoylated product was obtained from 1 g (0.004 mole) of the starting material; after recrystallization from absolute ethanol, the product had an m. p. of 148°. This substance is described here for the first time.

	Found %:	C 71.82; 71.91;	H 5.12; 5.15
$C_{41}H_{34}O_{10}$.	Calculated %:	C 71.72;	H 4.98

1-Phenyl-1-desoxygalactose. Deacetylation of the original tetracetate was carried out by the method described above. 1.71 g (65.3% of theoretical) of a crystalline product with an m. p. of 132° was obtained from 4.46 g (0.012 mole) of the starting material. The substance is described here for the first time.

	Found %:	C 59.87; H 6.93
$C_{12}H_{16}O_5$.	Calculated %:	C 60.00; H 6.67

1-Phenyl-1-desoxy-2,3,4,6-tetrabenzoylgalactose. Benzoylation of 1 g (0.004 mole) of 1-phenyl-1-desoxygalactose by the method described yielded 1.83 g (95.8% of theoretical) of crystalline benzoylated product with an m. p. of 40°. This substance is described here for the first time.

	Found %:	C 73.41; 73.37;	H 4.78; 4.64
$C_{40}H_{32}O_9$.	Calculated %:	C 73.17;	H 4.88;

1-Phenyl-1-desoxy-6-tritylglucose. 1 g (0.004 mole) of 1-phenyl-1-desoxyglucose was dissolved in 5 ml of pyridine, and to the solution was added 1.2 g of triphenylchloromethane. The solution was allowed to stand for two days at room temperature; it was then cooled with ice, and water was added dropwise until the solution became turbid. After half an hour, the solution, which had been cooled continuously during this time, was poured into 50 ml of ice water; this caused the separation of a thick oil, which was washed with water and dissolved in methanol. The soluble triphenylcarbinol was filtered, the filtrate was evaporated on a water bath, and the dry residue was recrystallized from methanol. The yield was 0.5 g (25% of theoretical).

1-Phenyl-1-desoxy-6-tritylglucose is a white crystalline powder with an m. p. of 110°. The substance is described here for the first time.

$C_{31}H_{32}O_5$.	Found %	C 76.98; 77.23; H 6.47; 6.33
	Calculated %	C 77.17; H 6.62

1-Phenyl-1-desoxy-6-tosylglucose. 2 g (0.01 mole) of p-toluenesulfonyl chloride was added to a solution of 0.5 g (0.002 mole) of 1-phenyl-1-desoxyglucose in 10 ml of pyridine. The solution was held for 2 hours in a thermostatted bath at 30°, and was then allowed to stand overnight. When the solution was poured into water, the tosylated product separated in the form of a syrup, which was extracted with chloroform. The chloroform extract was dried over calcium chloride; after evaporation of the solvent and recrystallization from absolute ethanol, there was obtained 0.47 g (57% of theoretical) of crystalline 1-phenyl-1-desoxy-6-tosylglucose, which decomposed at 165-170°. Sulfur determination by Messinger's method gave 7.62% (S calculated, 7.80%). The compound was soluble in pyridine, alcohol, and chloroform. This substance is described here for the first time.

6-Phenyl-1-gulonic acid. A solution of 2.2 g (0.009 mole) of 1-phenyl-1-desoxyglucose in a seven-fold amount of nitric acid (sp. gr. 1.15) was allowed to stand for 38 hours, after which it was evaporated on a water bath to the consistency of a syrup. The syrup was dissolved in a small amount of water and again evaporated. The resulting material was extracted with methyl acetate, the solution was evaporated to dryness, and the residue was subjected to a second treatment with nitric acid by the method described above. The resulting lactone of the acid was extracted by a prolonged contact with boiling ether. The lactone was obtained in the form of a thick transparent syrup upon distillation of the ether. The yield was 0.5 g (22% of theoretical).

This material is soluble in water, ether, methyl acetate, pyridine, and ethanol, and insoluble in benzene and toluene. It forms an insoluble lead salt.

$C_{13}H_{16}O_8$	Found %	C 56.43; H 6.08
	Calculated %	C 56.69; H 5.90

The acid equivalent, determined by titration with a base, was 248 (calculated, 254). The substance is described here for the first time.

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ON THE COMPOSITION OF THE KETONES FORMED DURING THE LIQUID-PHASE OXIDATION OF n-PARAFFINIC HYDROCARBONS

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We have shown in preceding investigations [1-3] that the chief products of the liquid-phase oxidation of n-paraffinic hydrocarbons with molecular oxygen under mild conditions (oxidation with a nitrogen-oxygen mixture containing 3.0-3.5% oxygen) and in the presence of boric acid are straight-chain secondary alcohols with the same number of carbon atoms in the molecule as the original hydrocarbon and comprising a mixture of all possible isomers with respect to the position of the hydroxyl group.

The by-products in this process comprise compounds with a carbonyl group, acids, and polyfunctional compounds; the study of the composition and structure of these products can yield additional information for the determination of the mechanism of the liquid-phase oxidation of n-paraffinic hydrocarbons with molecular oxygen. Since the carbonyl compounds constitute a considerable part of the total amount of by-products, we turned our attention first to a study of the composition and structure of these carbonyl compounds. n-Hexadecane was used as the feed to the oxidation process; it had a b. p. of 105.5-105.7°/1 mm, n_D^{20} 1.4344, d_4^{20} 0.7732; f. p. (cryst.) 16.6°.

TABLE 1

Characteristics of the Oxidates Obtained during the Oxidation of n-Hexadecane

Experimental values					Product distribution, mole %		
acid no.	ester no.	hydroxyl no.	carbonyl no.	total functional group content, mmole/g	free and combined acid	free and combined alcohols	compounds with carbonyl group
8.8	12.8	95.7	30.4	2.85	13.26	67.73	19.01
7.7	12.2	92.5	29.0	2.74	12.96	68.16	18.88
5.5	16.7	94.7	32.1	2.95	13.40	67.23	19.37
5.7	12.6	94.4	28.0	2.74	11.92	69.79	18.24
5.3	14.5	95.8	30.1	2.86	12.36	68.85	18.79

Oxidation of the n-hexadecane was carried out for 4 hours in a previously described apparatus [2] with a nitrogen-oxygen mixture containing 3.5% O_2 at a temperature of 165-170°; boric acid was added in an amount of 5% based on the original hydrocarbon. The feed rate of the oxidizing gas was 1000 liters/kg/hour.

Some properties of the oxidates are presented in Table 1; it may be seen from these properties that among the products formed during the oxidation of n-hexadecane under mild conditions in the presence of boric acid are

TABLE 2

Semicarbazone Melting Points (°C)

Methyl n-amyl ketone	123	Ethyl n-hexyl ketone	111-112
Methyl n-hexyl ketone	123	Ethyl n-heptyl ketone	100-101
Methyl n-heptyl ketone	119-120	Ethyl n-decyl ketone	90
Methyl n-octyl ketone	126(121)	Ethyl n-undecyl ketone	89
Methyl n-nonyl ketone	122-123	Ethyl n-dodecyl ketone	90.5
Methyl n-decyl ketone	122-123	Ethyl n-tridecyl ketone	88
Methyl n-undecyl ketone	126	Propyl n-amyl ketone	73-74
Methyl n-hexadecyl ketone	122	Propyl n-hexyl ketone	51-52
Ethyl n-butyl ketone	99-100	Octyl n-hexadecyl ketone	39-41

compounds containing a carbonyl group; these comprise about 19 mole % of the total amount of oxygen containing products.

The carbonyl compounds were separated from the oxidate in order to determine their composition. Since the oxidates gave a negative reaction for aldehydes (silver mirror test and fuchsin-sulfurous acid), separation of the carbonyl compounds present in the oxidates was carried out as follows. The oxidates from the first four experiments were combined, and the compounds not reacting with boric acid were distilled under vacuum. From 176 g of oxidate was obtained 105 g of distillate, which consisted chiefly of unreacted hydrocarbon and carbonyl compounds along with small amounts of acids, esters, and free alcohols. Analysis of the distillate gave the following results: carbonyl number, 30.3; acid number, 12.1; ester number, 8.1; hydroxyl number, 6.0.

It may be seen from these data that of the total amount of compounds with a carbonyl group present in the oxidate (94.31 milliequivalents of CO group), about 60% (56.71 milliequivalents of CO group) was present in the distillate, while 40% remained with the products reacting with boric acid; on this basis, it can be assumed that

TABLE 3

Fractionation of Esters Obtained during the Oxidation of Hexadecanones. 20.38 mmoles of esters and 60 g of chaser were used

b. t., °C	Wt. of fraction, g	Ester No. of fraction	Amount of ester, mmoles	Ag content of silver salt, %	Literature and calculated data: methyl ester of acid	Literature and calculated data: b. t. of individual CH_3 esters of acids and chaser	Literature and calculated data: calc. Ag content of silver salt of acid
758 mm Hg pressure							
62—95	1,46	0	—	—			
95—130	4,97	11,52	1,02	49,91	n-valeric	97—127	51,64
130—155	3,75	26,48	1,77	47,90	n-caproic	127—150	48,37
155—177	4,36	29,21	2,27	45,00	enanthic	150—175	45,51
2 mm Hg pressure							
38—55	4,75	23,50	1,99	42,35	n-caprylic	40—53	42,97
55—65	1,50	28,80	0,77	40,56	n-pelargonic	53—68	40,67
65—70	1,74	20,18	0,63	39,64			
70—75	1,06	22,01	0,77	38,73	n-capric	68—79	38,68
75—80	3,12	14,41	0,82	38,54			
80—90	3,25	26,58	1,54	36,86	undecanoic	79—92	36,82
90—95	2,82	17,90	0,90	35,34			
95—105	2,56	25,90	1,18	34,84	lauric	92—105	35,12
105—110	1,91	18,55	0,63	33,83	tridecanoic	105—117	33,58
110—120	3,74	22,41	1,50	32,78			
120—130	3,82	17,18	1,17	32,65	myristic	117—130	32,04
130—140	5,79	6,39	0,66	—	pentadecanoic	130—143	30,89
140—150	5,03	0,33	0,03	—			
Residue >150	5,72	—	—				

the carbonyl-containing compounds formed during the oxidation of n-hexadecane consist of ketones and polyfunctional compounds containing a carbonyl group (chiefly, keto alcohols). In order to determine the composition of the ketones present in the distillate, the latter was separated into paraffinic hydrocarbons and oxygen-containing compounds by chromatographing over ACK silica gel.

n-Pentane was used as the displacing liquid for the hydrocarbons, while methanol was used for the oxygen-containing compounds. Chromatographing of 95 g of distillate yielded 14.8 g of oxygenated compound concentrate with the following characteristics: carbonyl number, 162.5; hydroxyl number, 28.7; ester number, 41.2; acid number, 22.5. This concentrate was treated with a concentrated solution of a base in order to saponify the esters present, and it was then freed of alcohols by conversion of the latter to boric acid esters. As a result of these treatments, 8.8 g of carbonyl compounds was obtained, which, after distillation under vacuum, had a b.p. of 122-127°/1 mm and a carbonyl number of 226 (carbonyl number calculated for $C_{16}H_{32}O$, 233.0).

Elemental analysis of the carbonyl compounds:

	Found %	C 80.00;	80.01;	H 13.50;	13.57	
$C_{16}H_{32}O$.	Calculated %	C 79.93		H 13.41		

On the basis of the experimental data presented above, it can be concluded that the carbonyl compounds formed during the oxidation of n-hexadecane are chiefly hexadecanones. The semicarbazones of these ketones were prepared. Fractional crystallization from ethanol gave a crystalline product which melted in the range 124.5-125.5°. Elemental analysis of the semicarbazones:

	Found %:	C 68.87;	69.59;	H 11.80;	11.83	N 13.05;	13.02
$C_{17}H_{35}N_3O$.	Calculated %:	C 68.63;		H 11.86;		N 14.14	

In Table 2 are presented the melting points of semicarbazones in which the position of the carbonyl group varies [4]; a comparison of the melting points shows that the semicarbazones of the methyl ketones have melting points lying in the interval 120-126°, regardless of molecular weight. As the carbonyl group moves away from the end carbon atom, i.e., with a transition from methyl ketones to ethyl ketones to propyl ketones, etc., the melting point of the semicarbazones decreases. Consequently, the carbonyl compounds isolated from the products of the oxidation of n-hexadecane contain methyl n-tetradecyl ketone. However, the methyl n-tetradecyl ketone comprised only a small part of the total amount of semicarbazones obtained. Repeated crystallization of the mother liquor isolated a substance which did not have a sharp melting point. Therefore, it was not possible to form a final conclusion as to the composition of the ketones under investigation on the basis of the data obtained during the determination of the melting points of the semicarbazones. A method in which the ketones are oxidized with potassium dichromate in a medium of dilute sulfuric acid was used to solve this problem; this method has been described by us previously [3].

6 g of ketones, 18 g of potassium dichromate and 60 g of H_2SO_4 (48%) were used in the oxidation. The reaction yielded a concentrate of water-insoluble acids with an acid number of 328.5 and 1.4 g of neutral compounds with a carbonyl number of 189. These acids were converted to the corresponding methyl ester, which were distilled with a chaser in a column. The distillation results are presented in Table 3. The distribution of the acids was estimated from the boiling ranges of the individual fractions, the determination of the ester numbers of these fractions, and from the silver contents of the silver salts of the acids separated from these fractions; this distribution is shown in Table 4. It may be seen from the data presented in Table 4 that oxidation of the ketones with potassium dichromate in dilute H_2SO_4 yielded roughly equivalent amounts of acids* from C_6 to C_{14}; on the basis of these data, it may be concluded that the carbonyl group was present at different locations in the ketones investigated.

Thus, as a result of the present investigation it has been established that the carbonyl compounds formed during the liquid-phase oxidation of n-paraffinic hydrocarbons with molecular oxygen (in the presence of boric acid) are mainly ketones having the same chain length as the original hydrocarbon; the ketones are a mixture of

* The water-soluble acids were not investigated.

TABLE 4

Distribution of Acids Obtained by Oxidation of the Hexadecanones

Acid	Acid distribution according to Ag content of silver salts		Acid	Acid distribution according to Ag content of silver salt.	
	mmole	%		mmole	%
n-Valeric	0.51	2.90	Undecanoic	1.69	9.61
n-Caproic	1.99	11.30	Lauric	1.88	10.63
Enanthic	2.12	12.04	Tridecanoic	1.74	9.88
n-Caprylic	1.87	10.62	Myristic	1.65	9.38
n-Pelargonic	1.65	9.38	Pentadecanoic	0.65	3.68
n-Capric	1.86	10.58			

all theoretically possible isomers with respect to the position of the carbonyl group. In addition to the ketones, polyfunctional compounds containing a carbonyl group are formed.

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**In Russian.

ON THE INTERACTION OF TETRAALKYLDIHYDRIDISILOXANES WITH BIFUNCTIONAL UNSATURATED COMPOUNDS

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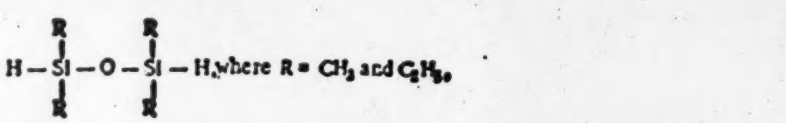
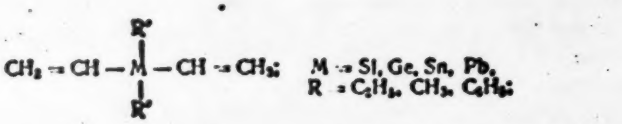
We have previously shown [1] that tetraalkyldihydridisiloxanes,

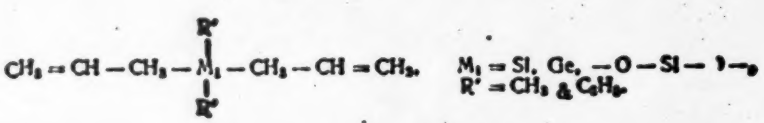


where R = CH_3 and C_2H_5,

react with acetylene at atmospheric pressure in the presence of a very small amount of an 0.1 M solution of chloroplatinic acid in isopropyl alcohol with the formation of polymeric products. The present work was devoted to an investigation of the interaction of these same disiloxanes with bifunctional unsaturated compounds of the types

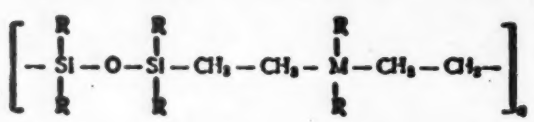


M = Si, Ge, Sn, Pb;
R = C_2H_5, CH_3, C_6H_5;

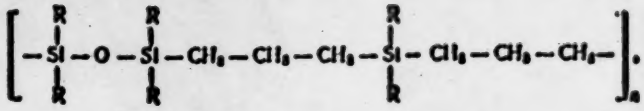


M_1 = Si, Ge, —O—Si—;
R' = CH_3 & C_6H_5.

Like the reaction with acetylene, the interaction of tetraalkyldihydridisiloxanes with the monomers indicated above was carried out in the presence of chloroplatinic acid. The reaction between equimolar amounts of the components resulted in the formation of polymers, which were obtained in the form of viscous oils in yields of up to 80%. The infrared absorption spectra, the data from elemental analyses, and the molecular weight determinations indicated that the molecules of these polymers consisted of the units



or, respectively,



where n = 2 – 15.

The results obtained in this investigation are presented in Table 1. As an examination of the table shows, the data from the elemental analyses are in good agreement with the calculated values.

The polymerization coefficient (n) did not exceed 15, and varied depending on the components used. It was established, for example, that n decreases with a change from tetramethyldisiloxane to dimethyldiethyldisiloxane, and decreases still more with a further change to tetraethyldisiloxane. The experiments showed that divinyl monomers are more active in this reaction than are diallyl monomers; the reaction proceeded most vigorously with diethyldivinylsiloxane, but was almost as vigorous with diethyldivinylgermane.

Diethyldivinyltin did not react, and diethyldivinyllead decomposed with the liberation of lead*.

It is worthy of note that the tetraalkyldihydridisiloxanes on which this reaction is based are readily available compounds; they are prepared in high yields by hydrolysis of dialkylchlorosilanes. The latter can be prepared in the laboratory by Grignard synthesis of methyl or ethyl chlorosilanes by close fractionation or by chemical methods [2]. The dialkylchlorosilanes obtained by Grignard synthesis can be hydrolyzed without separation from the reaction mixture.

EXPERIMENTAL

Preparation of the polymers. Equimolar amounts (0.12 mole) of the disiloxane and monomer were charged to a glass tube, and a thin-wall tube containing the catalyst (0.01 g of a decimolar solution of chloroplatinic acid in isopropyl alcohol) was placed on the bottom of the reaction tube. After the usual operations for removing the air while cooling the reaction mixture, the reaction tube was sealed, heated to 30-35°, and the tube containing the catalyst was broken by vigorously shaking the reaction tube.

After several minutes, an exothermic reaction was noted, and the reaction mixture gradually thickened. When the temperature of the reaction mixture had decreased appreciably, the reaction tube was placed in a thermostatted bath and heated at 120° for 6 hours. The reaction tube was then opened, and the contents were diluted with dry benzene and filtered to separate the polymer; the benzene was distilled under vacuum, and the residue was brought to constant weight at 120°/4 mm. Part of the benzene solution was mixed with a 5-fold amount of methyl alcohol; this resulted in the separation of an oil, which, after separation by decantation, was also brought to constant weight. The resulting polymers were then analyzed: the elemental composition and molecular weight (cryoscopically in benzene) were determined, and the infrared absorption spectra were obtained.

I. Synthesis of the tetraalkyldihydridisiloxanes. $H(C_2H_5)CH_3SiOSi(CH_3)(C_2H_5)H$. Ethylmagnesium chloride, obtained from 49 g (2 g atoms) of Mg in 1.5 liters of absolute ether, was added, over a period of 3 hours, to a solution of 650 g (5.65 mole) of methyldichlorosilane in 1.5 liters of ether; the reaction mixture was cooled and stirred well during the addition. The ether solution was separated from the solid material, and the latter was washed with ether. The ether and methyldichlorosilane were distilled, and 145 g of methylethylchlorosilane, b. p. 85-96°**, was obtained.

The yield, calculated on the magnesium used, was 67%.

200 ml of water was added dropwise, with effective stirring, to a solution of 120 g of $H(C_2H_5)(CH_3)SiCl$ in 500 ml of ether; after the evolution of heat had ceased, the reaction mixture was stirred for an additional 2 hours. The ether layer was separated, and the aqueous layer was extracted with 200 ml of ether. The ether extracts were washed and dried over calcium chloride, and the ether was distilled. Distillation of the ether yielded 79.5 g

* Synthesis of the diethyldivinyllead and its interaction with the disiloxane was carried out by M. D. Suchkova.
** Here and in the synthesis of II and III described below, the distillations were carried out in a column with 20 theoretical plates.

TABLE 1

Expt. No.	Composition of reaction mixture: monomer I	dihydridisiloxane, II	component ratio, I:II, mole	Polymer yield, wt. %	Polymer mol. wt., (average)	n	Elemental composition of polymer: found, % C	found, % H	found, % Si	calculated, % C	calculated, % H	calculated, % Si	Ratio of I to II in polymermolecules, assumed in calculation
1	Diethyldivinylsilane	Tetramethyldihydridisiloxane	1:1	57,6	2874	10	52,23 52,30	10,00 11,18	30,20 30,10	52,45	11,00	30,65	1:1
		Dimethyldiethyl-	1:1	79,7	2466	8			27,67 27,93			27,84	1:1
		Tetraethyl-	1:1	64,0	1997	6			25,62 25,31			25,48	1:1
2	Phenylmethyldivinylsilane	Tetramethyl-	1:1	61,0	4186	14	57,86 57,83	8,86 8,87	27,54 27,52	58,31	8,94	27,31	1:1
		Dimethyldiethyl-	1:1	58,0	3080	9	59,77 59,95	9,58 9,66	25,08 24,99	60,64	9,58	25,03	1:1
		Tetraethyl-	1:1	61,0	1968	5	62,38 62,29	10,01 9,80	23,01 23,08	62,56	9,97	23,10	1:1
		Tetraethyl-	1:1,5	70,0	900		60,59 60,52	10,07 10,17		61,13	10,48		2:3
3	Diethyldivinylgermane	Dimethyldiethyl-	1:1	80,6	6209	15	48,32 48,52	9,96 10,07		48,44	9,87		1:1
4	Dimethyldiallylgermane	Dimethyldiethyl-	1:1	70,0	4447	13	48,20 48,12	9,81 9,69		48,44	9,87		1:1
5	Diethyldivinyltin	Dimethyldiethyl-	1:1	No polymer obtained									
6	Diethyldivinyllead	Dimethyldiethyl-	1:1	Decomposition with the liberation of lead									
7	Diethyldiallylsilane		1:1	63,0	3016	9			26,07 26,27			25,48	1:1
		Tetraethyl-	1:1	81,0	1604	5	59,82 59,92	11,47 12,30	23,17 23,15	60,25	11,18	23,49	1:1
		Tetramethyl-	1,5:1	70,5	806				25,59 25,59			25,41	3:2
8	Diallyl	Dimethyldiethyl-	1:1	58,0	2190	9			22,09 22,89			22,97	1:1
		Tetraethyl-	1:1	43,0	1067	4	62,17 62,05	11,89 11,95	20,31 20,42	61,67	11,54	20,61	1:1
		Tetraethyl-	1:1,5	48,6	1593		60,72 60,65	11,92 11,85	21,60 21,54	60,31	11,81	21,70	5:6
9	Dimethyldiallylhydroxysilane	Tetraethyl-	1:1	79,3	1550	4	52,19 52,16	10,23 10,10	23,71 23,84	52,97	10,56	23,23	1:1
10	Diethyldiallylhydroxysilane	Tetraethyl-	1:1	71,4	527	2			21,70 21,93			21,56	1:1
11	Dimethyldiallylsilane	Tetramethyl-	1,5:1	88,0	641				28,27 28,28			28,51	3:2

of dimethyldiethyldihydridisiloxane with an m. p. of 125.5-126°; n_D^{20} 1.3980; d_4^{20} 0.7935; MR_D found, 49.3; calculated, 49.2. The yield was 88.5% of theoretical.

II. $H(C_2H_5)_2SiOSi(C_2H_5)_2H$. A) The synthesis was carried out in a manner similar to that described above; from 49 g (2 g atoms) of magnesium and 650 g (5 moles) of ethyldichlorosilane was obtained 214 g of diethylchlorosilane with a b. p. of 98.5-101.5°; n_D^{20} 1.4154; the yield was 88%.

The hydrolysis of the diethylchlorosilane was carried out in a manner similar to that used for I, and tetraethyldihydridisiloxane was obtained with a yield of 75-93%; b. p. 172-173°; n_D^{20} 1.4160; d_4^{20} 0.8159; MR_D found, 58.5; calculated, 58.3.

B) Grignard reagent, prepared from 49 g (2 g atoms) of magnesium and 235 g (2.15 mole) of ethyl bromide in 1 liter of ether, was added to 210 g (1.93 mole) of ethyldichlorosilane, and the reaction mixture was refluxed for 5 hours with stirring. After decomposition of the reaction mixture with water and the usual subsequent treatment, 57 g of triethylsilane with a b. p. of 105-106° and 81 g tetraethyldihydridisiloxane with a b. p. of 170-172°, n_D^{20} 1.4160, were obtained by distillation.

III. $H(CH_3)_2SiOSi(CH_3)_2H$. Methylmagnesium chloride, prepared from 49 g (2 g atoms) of magnesium in 1.5 liters of ether was added, over a period of 4 hours, to 172 g (1.5 moles) of methyldichlorosilane in 1.5 liters of ether; the reaction mixture was effectively cooled and stirred during the addition. After decomposition with water and the usual treatment, 38 g of tetramethyldihydridisiloxane with a b. p. of 70-71° was obtained by distillation; n_D^{20} 1.3700; d_4^{20} 0.7572; MR_D found, 40.1; calculated, 40.1. When the experiment was carried out under the same conditions but using 1.3 moles of methyldichlorosilane, the yield of $HMe_2SiOSiMe_2H$ was 24 g.

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THE ENERGY OF ACTIVATION OF THE DISSOCIATION OF ASSOCIATED ALKOXY DERIVATIVES OF TITANIUM

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We have previously reported that in dilute benzene solution, the degree of association of alkoxy derivatives of titanium rather slowly decreases with time and, after several hours, reaches unity [1]. The association of alkoxy derivatives of titanium is most naturally explained [2-5] by intermolecular coordination bonds between the oxygen atoms of one molecule and the titanium atoms of neighboring molecules.

In the present work, we investigated the temperature dependence of this phenomenon, and the activation energy of the dissociation of the association complexes was determined using, as before, a cryoscopic method. Figure 1 presents kinetic curves for the dissociation of tetra-n-propoxytitanium at various temperatures.

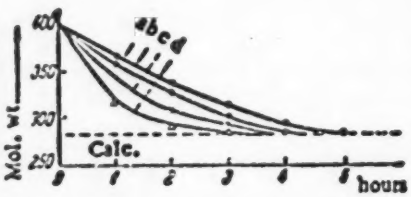

Fig. 1. Change in the molecular weight of $(n\text{-}C_3H_7O)_4Ti$ with time; benzene solution, 0.10 mole % concentration, at various temperatures: a) 10°; b) 17°; c) 25°; d) 35°.

Activation energies were calculated from the temperature dependencies of the initial dissociation rates (Fig. 2); these were found to be 7.7 kcal/mole in the case of tetra-n-propoxytitanium, 8.0 kcal./mole for associated tetraethoxytitanium, and 8.1 kcal./mole in the case of di-n-propoxytitanium oxide.

It is interesting to note that the limiting concentration at which the degree of association of alkoxy derivatives of titanium, which decreases with time, reaches unity does not depend to any great extent on the structure of the titanium compound (Fig. 3).

We also studied the effect on this phenomenon of the structure of the alkyl radical of the alkoxy titanium compound. The effect of steric hindrance on the degree of association of these substances was readily detected. When branching of the carbon chain of the tetraalkoxytitanium occured at the carbon atom closest to the titanium (tetraisopropoxytitanium, tetra-tert-butoxytitanium [2-6], association did not generally occur in benzene solution of up to 2.0 mole % concentration. In benzene solutions of tetraisopropoxytitanium of 1.296 and 1.988 mole % concentration, the molecular weights (immediately after dissolving the sample) were, respectively, 276 and 275 (calculated, 284).

When branching of the alkyl chain of the tetraalkoxytitanium occured at the β- or γ-carbon atom, the tetraalkoxytitanium was associated in benzene solution, and, just as in the case of substances containing alkyl groups of normal structure, their degree of association in dilute benzene solution decreased with time and reached unity.

Thus, the molecular weight of $[(CH_3)_2CHCH_2O]_4Ti$ in benzene solutions of 0.367 and 0.348 mole % concentration was found to be 460 and 453, respectively, immediately after solution of the substance. Subsequent determinations after 18 hours gave values of 336 and 349 (calculated, 340).

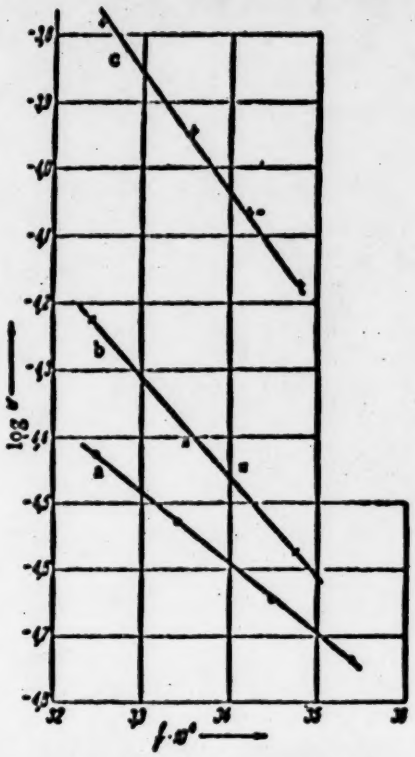

Fig. 2. Temperature dependence of the initial dissociation rates of complexes of $(n\text{-}C_3H_7O)_4Ti$ (a), $(C_2H_5O)_4Ti$ (b), and $(n\text{-}C_3H_7O)_2TiO$ (c).

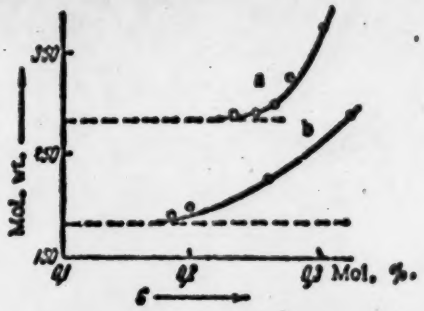

Fig. 3. Dependence on concentration of the molecular weights of $(n\text{-}C_3H_7O)_4Ti$ (a), and $(nC_3H_7O)_2TiO$ (b) determined after the solutions had stood for 18 hours at 20-22°. Broken line – calculated molecular weight.

The molecular weight of $[(CH_3)_2CHCH_2CH_2O]_4Ti$ in 0.251 mole % benzene solution was 400 immediately after solution of the sample, and this decreased to 331 (calculated, 396) after 18 hours.

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A COMBINATION METHOD FOR THE INVESTIGATION OF THE DETAILED HYDROCARBON GROUP COMPOSITION OF CRACKED GASOLINES

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The investigation of the group and individual hydrocarbon composition of the products of thermal and catalytic processing of petroleum distillates is of both scientific and practical interest. The unsaturated and other liquid hydrocarbons produced by these processes are most important resources. Of considerable interest, both from the point of view of theory and from the point of view of commercial practice, is the study of the question of the effect of the chemical composition of the raw feed to thermal or catalytic cracking on the composition and structure of the hydrocarbons obtained from these processes. An understanding of the nature of the hydrocarbons composing the cracked products requires the development of a reliable method for the investigation of both their individual and their detailed hydrocarbon group composition.

The chromatographic method developed by the present authors makes possible the separation of cracked gasoline into paraffinic-naphthenic, unsaturated, and aromatic hydrocarbons. The combination of the chromatographic method of separation with hydrogenation-dehydrogenation catalysis and with optical methods makes it possible to investigate both the individual [2-4] and the group chemical composition of cracked gasolines [5].

The present investigation describes a combination method which includes chromatographic separation of standard fractions (60-175°) of cracked gasoline into hydrocarbon classes combined with hydrogenation-dehydrogenation catalysis. This method permits the determination of the chemical composition of individual fractions with respect to seven sub-groups of saturated and unsaturated hydrocarbons.

EXPERIMENTAL

Pressure distillates of three samples of gasolines produced by thermal and catalytic cracking of distillates from Surakhany high-grade naphthenic petroleum* were used both for the development of the method and as objects of investigation.

1. Catalytically cracked gasoline (B-12) obtained from a kerosene-gas oil fraction (235-360°) by passage over silica-alumina catalyst at a temperature of 460° and a weight rate of 1.0.

2. Thermally cracked gasoline (B-2) obtained from a residuum (above 360°) at a temperature of 515° and a pressure of 38-40 atm.

3. Thermally cracked gasoline (B-11) obtained from a kerosene-gas oil fraction (235-360°) at a temperature of 515° and a pressure of 40 atm. These gasolines were distilled in a column of 30 theoretical plates, and the following fractions were collected: up to 60°, 60-95°, 95-122°, 122-150°, and 150-175°. Each fraction was separated chromatographically into naphthenic-paraffinic, unsaturated, and aromatic hydrocarbon fractions.

*The gasoline samples were prepared at the Experiment Station of the Azerbaidzhan Scientific Research Institute of the Petroleum Industry (Baku).

TABLE 1

Group Composition of Narrow Fractions of Gasolines (60–175°)

Properties of fractions	Gasoline-12				Gasoline-2				Gasoline-11			
	boiling range of fraction, °C											
	60–85	85–122	122–150	150–175	60–85	85–122	122–150	150–175	60–85	85–122	122–150	150–175
Paraffinic-naphthenic												
Yield, in wt. %	57,2	42,3	29,1	36,3	49,3	49,8	50,7	50,5	36,9	38,8	37,4	42,5
n_D^{20}	1,3948	0,4152	1,4259	1,4350	1,3883	1,4030	1,4141	1,4233	1,3920	1,4069	1,4190	1,4229
d_4^{20}	1,7061	0,7514	0,7705	0,7893	0,6895	0,7197	0,7428	0,7612	0,7005	0,7297	0,7547	0,7775
Aniline point	56,6	53,8	59,0	62,4	62,1	63,7	66,1	69,1	58,3	60,0	62,4	64,5
Unsaturated												
Yield, in wt. %	37,7	23,7	9,5	4,5	49,6	45,1	39,1	36,5	50,6	41,6	43,7	38,0
n_D^{20}	1,4120	1,4375	1,4410	1,4480	1,4085	1,4261	1,4349	1,4403	1,4092	1,4271	1,4342	1,4421
d_4^{20}	0,7221	0,79	0,7903	not det.	0,7156	0,7558	0,7756	0,7831	0,7209	0,7621	0,7740	0,7894
Aniline point	18,5	11,0	25,9	not det.	21,5	24,0	30,0	38,0	—	—	—	—
Mol. wt.	90,8	108,2	119,0	131,0	91,6	106,4	118,6	134,6	89,5	108,0	119,5	136,0
Iodine No.	291,8	283,6	278,0	260,0	289,0	293,0	259,0	220,0	299,0	256,0	242,0	213,0
Aromatic												
Yield, in wt. %	5,1	34,0	61,4	59,7	1,1	5,1	10,2	12,8	12,5	19,6	18,9	19,5
n_D^{20}	1,4959	1,4960	1,4979	1,5011	—	1,4900	1,4938	1,5000	1,4933	1,4935	1,4950	1,5011
d_4^{20}	0,8816	0,8667	0,8668	0,8733	—	0,8578	0,8612	0,8737	0,8735	0,8641	0,8639	0,8757
Iodine No.	23,3	5,5	5,5	12,0	—	35,7	27,5	27,3	13,0	7,2	17,0	35,5

TABLE 2

Detailed Hydrocarbon Group Composition of Narrow Gasoline Fractions

Hydrocarbons	Contents in wt. % of initial fraction																			
	gasoline-12					gasoline-2							gasoline-11							
	boiling range of fraction, °C																			
	60–85	85–122	122–150	150–175		60–85	85–122	122–150	150–175		60–85	85–122	122–150	150–175		60–85	85–122	122–150	150–175	
Cyclohexanes	2.8	13.6	0.8	10.4		3.3	8.3	7.3	5.4		3.7	10.0	7.8	9.8						
Cyclopentanes	17.8	13.4	7.3	10.5		7.5	10.4	10.1	6.7		8.5	8.6	9.4	10.4						
Paraffins	36.6	15.3	12.0	15.4		38.4	31.1	33.3	33.5		29.7	20.2	20.2	22.3						
Aromatics	5.1	34.0	61.4	59.7		1.1	5.1	10.2	12.8		12.5	10.6	18.9	10.5						
Cyclohexenes	1.0	3.8	1.7		4.0	2.0	6.3	7.2	6.3		3.6	9.7	8.3	7.9						
Cyclopentenes	10.5	11.4	3.5			9.7	13.3	9.1	4.9		10.7	9.5	9.2	6.6						
Alkenes	28.2	8.5	4.3			37.9	25.5	22.8	25.3		28.3	22.4	24.1	24.2						

In order to obtain comparable data and to obtain sufficient amounts of the respective fractions, identical fractions of the gasoline were chromatographed from 3 to 4 times. The yields of paraffinic-naphthenic, unsaturated, and aromatic fractions were determined as the average from 2-3 experiments (the divergence between experiments did not exceed 1%).

The contents of paraffinic -naphthenic, unsaturated, and aromatic hydrocarbons in the intermediate fractions were determined by calculation or by a second separation of these fractions using a small chromatographic column (the intermediate fractions constituted 3-5% of the fraction charged to the chromatographic column. The properties and group compositions of narrow fractions of gasolines 12, 2, and 11, isolated chromatographically, are presented in Table 1. The unsaturated fractions were hydrogenated in small autoclaves at a hydrogen pressure of 75-80 atm., a temperature of 150-200°, and in the presence of a catalyst (nickel on kieselguhr). 15-25 ml of the fraction was used in the hydrogenation.

The paraffinic-naphthenic fractions isolated chromatographically and the hydrogenation products obtained from the hydrogenation of the unsaturated fractions were subjected, after characterization, to analytical dehydrogenation over a catalyst – iron-promoted platinized carbon [7] – prepared by the method described by Musaev and Gal'pern [8].

The dehydrogenation was carried out at 300-302°, a space rate during the first dehydrogenation of 1:1, then 0.5:1 in individual cases, and 0.3:1 during the third dehydrogenation. The resulting catalyzates were characterized, after which they were sulfonated using Kaltwinkel's solution (30 g P_2O_5 + 100 ml of H_2SO_4). The content of aromatic hydrocarbons formed from cyclohexanes during the dehydrogenation and the content of pentamethylene hydrocarbons in the dearomatized catalyzate were determined by the aniline point method, while the content of paraffinic hydrocarbons was determined by difference. The detailed group composition of each fraction was calculated on the basis of the experimental data. The summarized data on the detailed hydrocarbon group composition of the fractions of the three gasolines are presented in Table 2.

As may be seen from Table 2, the catalytically cracked gasoline (B-12) differed from the thermally cracked gasolines by an increased concentration of aromatic hydrocarbons and by a sharply decreased concentration of unsaturated hydrocarbons. Gasoline-12 also differed from Gasolines 2 and 11 by an increased concentration (particularly in the first two fractions) of cyclopentanes and a decreased concentration of paraffins and alkenes with an insignificant concentration of cyclohexenes.

Gasoline-2 closely approximated gasoline-11 in chemical composition. The main difference between gasoline-2 and gasoline-11 was an increased amount of paraffinic hydrocarbons and a sharply decreased concentration of aromatic hydrocarbons. The concentration of olefinic hydrocarbons was very close to the same in these two gasolines.

Thus, by a combination of chromatographic separation with hydrogenation-dehydrogenation catalysis and the use of the aniline point method, there has been developed a combination method for the investigation of the detailed group composition of cracked gasolines. The proposed method makes it possible to carry out a differential characterization of the quantitative composition of each fraction separately with respect to seven sub-groups of saturated and unsaturated hydrocarbons. The data presented show the differences in the chemical composition of the gasolines investigated; these differences are connected with differences in the chemical composition of the raw feed and with the processing methods used.

T. N. Buturlova participated in this work.

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ON THE STATE OF THE ELEMENTS OF THE MIDDLE OF THE FOURTH PERIOD IN HYDROCHLORIC ACID SOLUTIONS

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(Presented by Academician L. I. Chernaev, July 13, 1959)

Ion exchange is widely used for the separation of metals in the analysis of various ores and alloys. Moreover, if cation exchange resins are used for the separation of mixtures of elements of Groups I-IV and anion exchange resins are used for the separation of mixtures of elements of Groups V-VIII, the separation of ions more closely related in properties is based chiefly on their different tendencies toward complex formation. In this connection, ion exchange has acquired an even greater significance as a method for the study of the states of elements and the stability and composition of their complex compounds in acid solutions. This is possible owing to the fact that simple cations of the metals are absorbed from solutions by the active groups of the cation exchangers, while their complex anions are absorbed by the active groups of anion exchangers.

The investigation of the states of elements in hydrochloric acid solutions is very interesting, since, according to the available data [1-8], ion exchange sorption of even the more closely related elements can differ considerably owing to the non-uniform stability of the chloride complexes.

The present work was devoted to a systematic investigation, by means of ion exchange, of the states of the elements of the middle of the fourth period in hydrochloric acid solutions. With this aim, distribution coefficients of the elements between ion exchange resins and hydrochloric acid solutions with HCl concentrations of from 0.1 to 10 N were determined. The elements studied were Cr (III), Mn (II), Fe (III), Co (II), Ni (II), and Cu (II), which are typical complex formers [9], and also Ti (IV).

Determination of the distribution coefficients was carried out by a widely used method [1]: an accurately weighed portion of the air-dried ion exchange resin was agitated with a specific volume of the solution under investigation until equilibrium was approached; aliquot portions of the solution were then taken, and the amount of element not sorbed by the resin was determined by the appropriate colorimetric method [10, 11]. The distribution coefficient was calculated by means of the equation

$$\rho = \frac{M_1}{M - M_1} \cdot \frac{v}{m},$$

where M_1 is the amount of the element sorbed by the ion exchanger, M is the total amount of the element in the original solution, v is the volume of solution used in the investigation, and m is the weight of ion exchanger. In our experiments, v was 50 ml and m was 0.5 g.

The original solutions were of the following concentrations: Ti (IV), 0.1197; Cr (III), 0.1733; Mn (II), 0.2784; Fe (III), 0.1861; Co (II), 0.2947; Ni (II), 0.2935; and Cu (II), 0.4765 mg/ml.

The sorbents used were strongly acid unifunctional cation exchangers KU-2 and SBS, strongly acid multifunctional cation exchanger KU-1, and anion exchange resin AN-2F. Preliminary to the work, the ion exchange resins were washed free of impurities, the cation exchange resins were converted to the H form, and the anion exchange resin was converted to the Cl form.

The results of the determinations of the distribution coefficients are presented in Table 1.

It is well known that the amount of cations absorbed by cation exchange resins decreases with a decrease in the pH of the medium [12]. However, the decrease in the sorbability of elements in hydrochloric acid solutions by cation exchangers cannot be explained only by the change in pH, since the formation of chloride anionic or neutral complexes is important here.

It may be seen from the data in Table 1 that in comparatively dilute solutions of hydrochloric acid (0.1-0.5 N), all of the elements studied were sorbed to a considerable extent by the cation exchangers. Consequently, they are present in the solutions in the form of simple cations: Ti^{4+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}. With an increase in the acidity of the solutions, ion exchange sorption of the elements rapidly decreased, which (along with the increased concentration of hydrogen ions) can be explained by the formation of anion complexes. The data of Table 1 show that beginning with the 6 N hydrochloric acid solution, Co (II) is converted to chloride-containing complex anions and is sorbed by the anion exchange resin. With Ti (IV) and Fe (III), the formation of anion complexes was noted beginning with hydrochloric acid solutions of 8 N concentration. With regard to Mn (II), Ni (II), and Cu (II), the complete absence of sorption by the anion exchanger excludes the possibility of the formation of anion complexes by these elements under the present conditions of acidity. Apparently, beginning with approximately a 2 N concentration of HCl, these elements exist in the form of neutral complexes, if such complexes are sufficiently stable.

TABLE 1

Distribution Coefficients φ of Elements in Hydrochloric Acid Solutions

Normality of the HCl	Ti	Mn	Fe	Co	Ni	Cu
			On KU-2			
0,1	324,61	292,96	3726,06	286,54	256,12	335,44
0,5	22,47	22,45	111,88	32,09	40,03	4,78
1	1,95	0	0,75	0	5,90	0,74
2	0	0	0	0	0	0
4	0	0	0	0	0	0
8	0	0	0	0	0	0
			On SBS			
0,1	156,26	72,46	1007,07	74,89	169,01	93,65
0,5	30,49	14,79	49,47	31,62	29,01	8,48
1	0	2,49	7,79	4,72	21,07	7,43
2	0	0	0	0	9,14	0
4	0	0	0	0	5,92	0
8	0	0	0	0	2,28	0
			On KU-1 (espatite-1)			
0,1	344,48	48,93	877,41	61,73	187,76	65,78
0,5	20,68	2,19	59,19	19,18	18,49	3,27
1	2,22	0	16,61	1,97	10,54	1,47
2	0	0	0	0	10,16	0
4	0	0	0	0	—	0
8	0	0	0	0	—	0
			On AN-2F			
0,1	0	0	0	0	0	0
0,5	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0	0	0	0
4	0	0	0	0	0	0
6	0	0	0	8,78	0	0
8	14,76	0	26,94	36,90	0	0
10	108,42	0	79,63	61,19	0	0

We obtained no new data differing from that available in the literature relative to the state of chromium (III) in hydrochloric acid solutions [3]. At HCl concentrations above 2 N, chromium was not sorbed either by the cation exchangers or by the anion exchanger. Since it is one of the most typical complex formers, it too probably formed neutral complexes.

The data obtained in the present investigation can have a practical significance in the separation of elements of the middle of the fourth period by means of column chromatography. It is evident that each of the metals which form anion chloride complexes (Ti, Fe, Co), can be separated from chromium, manganese, nickel, and copper by anion exchange resins if the hydrochloric acid solution is sufficiently concentrated (8 N and higher).

Separation with cation columns is possible with solutions in which the ratios of the distribution coefficients of the individual pairs of metal are comparatively high.

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LIQUID-PHASE OXIDATION OF OLEFINS IN THE PRESENCE OF BORIC ACID

Corresponding Member AN SSSR A. N. Bashkirov and Shiman Pal

Investigations carried out in our laboratory on the liquid-phase oxidation of hydrocarbons [1, 2] have shown that in the initial stage of the oxidation of paraffinic hydrocarbons of normal structure – in the stage leading to the formation of alcohols – destruction of the original hydrocarbon molecule does not occur. Under our conditions, including the presence of boric acid, the reaction products were predominantly secondary alcohols, a mixture of all possible isomers having the same number of carbon atoms in the molecule as the original hydrocarbon. These isomeric alcohols were formed in equimolar amounts. This provides a basis for the assumption that the reactivity with respect to oxygen of the secondary carbon atoms of molecules of higher normal paraffinic hydrocarbons is practically uniform. The oxidation products of normal paraffinic hydrocarbons contained no primary alcohols having the same number of carbon atoms in the molecule as the original hydrocarbon. This can apparently be explained by the greater stability of the C-H bond in a methyl group as compared to that of a C-H bond in a methylene group.

TABLE 1

Characteristics of Oxidates

Time, min	Analysis of oxidate, number					Conversion, mole %	Product distribution in oxidate, mole, %		
	iodine	acid	ester	carbonyl	hydroxyl		acids	CO compounds	alcohols
30	130,0	—	—	11,8	46,0	17,3	—	20,4	79,6
60	129,0	—	—	15,0	53,6	20,6	—	21,8	78,2
90	128,0	0,5	2,0	16,1	60,9	23,8	3,1	19,8	77,1
120	124,2	1,2	4,8	15,3	67,2	26,5	6,4	16,4	77,2
180	121,0	2,8	12,2	15,1	72,4	30,7	13,1	13,2	73,7

The study of the liquid-phase oxidation of olefins is of considerable interest for an understanding of the mechanism of hydrocarbon oxidation and the effect of the structure of the hydrocarbon molecule on the nature of the oxidative conversion of the hydrocarbons. In this connection, we carried out the oxidation of 1-dodecene in the presence of boric acid; the 1-dodecene was obtained by Grignard synthesis and had a b. p. of 212-213°(753 mm); d_4^{20} 0,7583; n_D^{20} 1,4301; iodine number, 149.1.

The oxidation was carried out at ordinary pressure with a nitrogen-oxygen mixture containing about 4% O_2; the specific feed rate of the oxidizing gas was about 800 liters/kg. The amount of boric acid added was 5-7% of the original hydrocarbon. The reaction temperature was 165-175°, and the run duration was 2-3 hours. The oxidation was carried out in an apparatus described previously [1].

The composition of the oxidates are shown as a function of time in Table 1.

TABLE 2

Characteristics of the Hydroxyl-Containing Compounds Obtained by Oxidation of 1-Dodecene

Fract. no.	Physical constants						Literature and calc. data				
	b. p. at 1 mm Hg, °C	n_D^{20}	hydroxyl no.	iodine no.	alcohol content		compound	hydroxyl no.	iodine no.	b. p. at 1 mm Hg, °C	n_D^{20}
					primary	sec.					
1	64.5–65.0	1.4334	347	1.5	92	8	1-Nonanol	358.5	0	63.2 (*)	1.43347 (*)
2	85.0–85.5	1.4493	301	33.2	1	99	1-Dodecenol	304	137.8	—	—
3	125.0–135.0	—	526	11.3	—	—	1,2 Dodecanediol	556	0	—	—

*The product to be analyzed was first hydrogenated using Raney nickel catalyst. Determination of the contents of primary and secondary alcohols was carried out by a method developed by us and previously described [9].

The data presented show that alcohols constitute the major product of the conversion of 1-dodecene, comprising about 75 mole % at an oxidation depth of about 27%.

The oxidate was treated with water at 95° to decompose the boric acid esters. Esters, which were present in small amounts, were saponified with an alcoholic solution of KOH. Chromatography over ASK silica gel was used to separate the oxygen-containing compounds from the unreacted hydrocarbon. Petroleum ether and methanol were used as displacing liquids. The resulting hydrocarbon was distilled and again oxidized. The alcohols, of which 41 g was obtained, were purified from ketones through the boric acid esters, after which they were distilled under vacuum. They had a hydroxyl number of 330 and an iodine number of 33.2. Three main fractions boiling at 64.5-5.66°, 82-85°, and 125-135° were separated by distillation in a rectification column at an absolute pressure of 1 mm Hg. The first two fractions were liquid, while the third was a crystalline material. The characteristics of these fractions are presented in Table 2.

TABLE 3

Distribution of Acids

Acid		Mole %
Valeric	$C_5H_{10}O_2$	4.7
Caproic	$C_6H_{12}O_2$	8.1
Enanthic	$C_7H_{14}O_2$	8.9
Caprylic	$C_8H_{16}O_2$	10.0
Pelargonic	$C_9H_{18}O_2$	40.5
Capric	$C_{10}H_{20}O_2$	23.0
Undecanoic	$C_{11}H_{22}O_2$	4.8

On the basis of the data presented in Table 2, it can be stated that the first fraction, which comprised 38% of the total hydroxyl-containing compounds, was n-nonyl alcohol. For proof of this conclusion, the phenylurethan with an m. p. of 61-62° (calculated, 62°) [6] was prepared; its analysis is presented below:

Found %: C 72.82; H 9.58; N 5.28
Calculated %: C 72.96; H 9.57; N 5.32

A mixture of the phenylurethan with a known sample of n-nonanol phenylurethan melted without depression of the melting point.

In addition to its high hydroxyl number, the second fraction was characterized by a high iodine number. The results of the analysis of this fraction confirmed that it consisted predominantly of secondary unsaturated alcohols, $C_{12}H_{23}OH$. For the determination of the position of the hydroxyl group in these alcohols, we used a method, previously described, in which the alcohols were oxidized with potassium dichromate in a medium of dilute H_2SO_4 with subsequent identification of the resulting acids [2]. The alcohols investigated were preliminarily subjected to selective hydrogenation over Raney catalyst at a temperature of 180° and 30 atm in a medium of n-heptane.

As a result of this investigation, a number of acids were isolated and identified; their distribution is presented in Table 3.

The experimental data presented above show that the alcohols of this fraction were a mixture of isomers of secondary unsaturated alcohols in which about 60 mole % was 3-dodecenol. The remaining 40 mole % was the other possible isomers of secondary unsaturated alcohols, $C_{12}H_{23}OH$.

The alcohol of the third fraction obtained during the distillation of the alcohols was a crystalline substance. Recrystallization from petroleum ether gave snow-white crystals with an m. p. of 57.5-58.0° (literature value, 56-58° [7]). The hydroxyl number was 555 (calculated, 556).

B. 1,2-dodecanediol.	Found %:	C 71,21; H 13,0
	Calculated %:	C 71,43; H 12,05

The data presented above and also a qualitative reaction for glycols with adjacent hydroxyl groups [8] provided confirmation that this substance was 1,2-dodecanediol. Thus, in the liquid-phase oxidation of 1-dodecene in the presence of boric acid, three main products are formed (in about 70% yield): primary n-nonyl alcohol, a mixture of isomeric secondary dodecenols, and 1,2-dodecanediol; these products were formed in a ratio of 2,2:1:0,8.

In addition to the work just described, we also oxidized 2-dodecene under the same conditions; the 2-dodecene was obtained by Grignard synthesis and had a boiling point of 86-87° at 3 mm Hg; d_4^{20} 0.7601; n_D^{20} 1.4303 and an iodine number of 151. We limited this investigation to the isolation of octyl alcohol from the oxidate. The n-octyl alcohol was identified as the phenylurethan. The characteristics of the n-octyl alcohol and its phenylurethan are shown in Table 4.

TABLE 4

	Alcohol			Phenylurethan			
				elemental composition, %			
	b. p. at 1 mm Hg	hydroxyl no.	n_D^{20}	m. p., °C	C	H	N
Found	54,0—56,5	428	1,4300	73—74	72,21	9,24	5,59
Lit. and calc. data	54,0 (*)	430	1,4292(*)	74	72,25	9,30	5,62

Thus, it may be seen from the experimental data presented above that the presence of a double bond in the hydrocarbon molecule has a substantial effect on the course of the oxidation process. While the oxidation of n-paraffinic hydrocarbons yields secondary alcohols with the same number of carbon atoms in the molecule as the original hydrocarbons, the main course of the oxidative conversion of olefins under the same conditions is a reaction leading to the formation of primary alcohols with fewer carbon atoms in the molecule, rupture of the C-C bond occurring between the carbon atoms α and β to the double bond.

In addition to the main reaction forming primary alcohols, during the oxidation of olefins a reaction also occurs, though to a lesser extent, which leads to the formation of unsaturated secondary alcohols with the same number of carbon atoms in the molecule as in the original olefins and with retention of the double bond. These alcohols are a mixture of isomers; about 60 mole % of the mixture is an alcohol in which the hydroxyl group is alpha to the double bond of the original olefin. A glycol with the same number of carbon atoms in the molecule as the original olefin and in which the hydroxyl groups are on adjacent carbon atoms at the site of the double bond of the olefin is formed during the oxidation.

Thus, the presence of a double bond in a hydrocarbon molecule has a substantial effect on the strength of the C-C bonds between the alpha and beta atoms of the molecule (with respect to the double bond); as a consequence, rupture of this bond takes place with the formation of primary alcohols with fewer carbon atoms in the molecule. The presence of the double bond also has an effect on the strength of the C-H bonds of the secondary carbon atoms. Therefore, the most reactive carbon atom is one alpha to the double bond.

The presence of glycol in the reaction products provides a basis for the assumption that the oxidation of olefins can, to a certain extent, involve the double bond, like the Prilezhaev reaction. All of the material

above shows that the structure of the hydrocarbon molecule has a decisive effect on the course of the oxidative conversion of hydrocarbon molecules and, as a consequence, on the composition of the oxygen-containing compounds formed during the oxidation.

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INHIBITION OF THE CHAIN DECOMPOSITION OF POLYMERS BY DISRUPTING STRUCTURAL HOMOGENEITY THROUGH COPOLYMERIZATION

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It is well known the addition to a monomer A of a small amount of a more readily polymerizable monomer B has an inhibiting effect on polymerization [1]. This fact can be explained on the basis that the radical ~B° at the end of the growing chain has little reactivity with respect to the main monomer A. The introduction into monomer B of a certain amount of the less reactive monomer A has no substantial effect on polymerization kinetics. The basic regularities specific for radical polymerization processes can also appear during thermal decomposition of polymers by a chain mechanism. It would be expected that the introduction into the homopolymer chain of small amounts of a component having a different activity (A or B) would cause some inhibition of the thermal decomposition of the polymer.

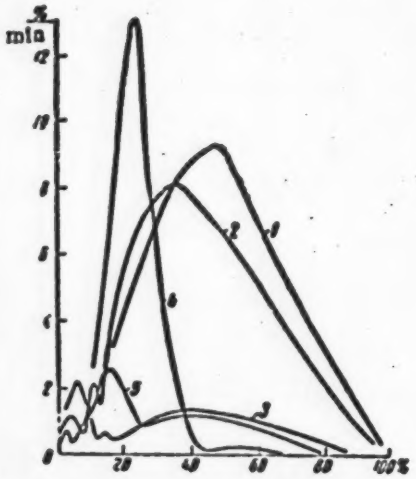

Fig. 1. Kinetics of the destruction of methyl methacrylate copolymers under vacuum at 368°: 1) PMMA, 2) copolymer of MMA + 1.52% MAA, 3) copolymer of MMA + 15% MAA, 4) polymethacrylic acid, 5) copolymer of MMA + 20% MMAm.

In the case of the chain thermal decomposition of a homopolymer as ~A–A–A–A→A + . A–A–A~ each elementary act of cleavage of a monomer molecule from the polymer chain is accompanied by the formation of a polymer free radical of the same type. Let us consider the case of the thermal decomposition of a polymer chain of A units containing a certain amount of B units, assuming that the radicals ~A° and ~B° differ substantially in reactivity: ~A–A–A°–B°–A–A~→chain decomposition. If the radical ~B° is the more reactive, then the energy required to split off the A° unit is not just the energy liberated during the addition of an A unit during polymerization, but also includes an additional amount of energy equal to the difference in the energies ~B° – ~A° . B. In this case, decomposition is retarded at the stage ·A°–B°–A–A–A~. If the radical ~B° is less reactive than the radical ~A°, then, by the same considerations, decomposition of the chain is retarded at the stage ·B°–A°–A–A–A~. Consequently, the introduction of even a small number of foreign monomer units into a macromolecule which decomposes by a chain mechanism must lead to an appreciable inhibition of thermal decomposition, and this inhibition effect will be greater, the greater the difference between the radicals ~A° and ~B° with respect to their reactivity.

These considerations are confirmed by experimental data obtained during a study of the thermal decomposition of copolymers of methyl methacrylate (MMA) with methacrylic acid (MAA), methyl methacrylamide (MMAm), and other monomers.

Fig. 2. Kinetics of the destruction of methyl methacrylate copolymers in air at 200°: 1) PMMA, 2) copolymer of MMA with citraconamide (40%), 3) same with methyl methacrylamide (40%), 4) same with hydroxymethyl methacrylamide (7%), 5) same with methacrylic acid (15%).

Thermal decomposition of the polymers was characterized by the kinetics of the evolution of gaseous decomposition products by a previously described method [2].

As follows from Fig. 1, the introduction into the polymethyl methacrylate chain of only 1.5% MAA units had an effect on the kinetics of the decomposition of the polymer (Curves 1 and 2). This suggests that the length of the kinetic chain in the depolymerization of PMMA homopolymer is about 100, and the introduction of an insignificant amount of hetero units inhibits chain decomposition. When the MAA content of the copolymer was increased to 15%, there was considerable suppression of chain decomposition; the decomposition rate decreased by a factor of approximately 8 as compared to the homopolymer decomposition rate (Fig. 1, Curves 1 and 3). The picture was similar in the case of the copolymer of MMA with methyl methacrylamide (Fig. 1, Curve 5).

The complex course of kinetic Curves 2, 3, and 4 at the beginning of the decomposition process merits attention. As shown previously [3], the appearance of the maxima, most sharply expressed in the case of PMAA homopolymer (Curve 4) is connected with cyclization of neighboring methacrylic acid units with the elimination of water and the formation of methacrylic anhydride.

It is well known that at high temperature (200° and above) in air, there is rapid chain decomposition of PMMA, which is initiated by oxidation reactions [2, 4]. As follows from the data presented in Fig. 2, the introduction of hetero units into the PMMA molecule sharply inhibits (by a factor of approximately 10) the thermal destruction of the polymer, and the chemical nature of the hetero units studied exerts no specific effect at all on the kinetics of the destruction process. It is evident that the increase in thermal stability of the polymers is linked only with the transition from homopolymer to copolymer.

The method previously used [2] for the inhibition of chain decomposition of PMMA by the addition to the polymer of certain vinyl derivatives which are capable of adding to the PMMA macroradical with the formation of a new, much less active macroradical is one case of the phenomenon considered here.

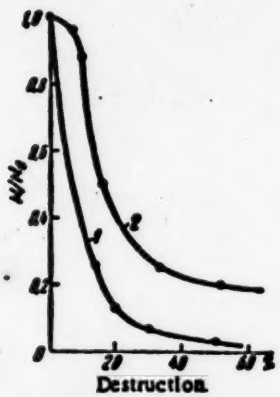

Fig. 3. Change in molecular weight during thermal decomposition of copolymers of MAA and MMA: 1) copolymer of MMA + 15% MAA, 2) copolymer of MMA + 1.5% MAA.

Since initiation of the thermal decomposition of PMMA proceeds chiefly by rupture of C–C bonds inside the chain [2], it can be assumed that in the cases of the copolymers studied in the present work, initiation of thermal destruction proceeds at the same rate for each copolymer, and the difference in the kinetics of the process must be due merely to a difference in the length of the kinetic chains.

Direct experimental proof of this assumption is presented in Fig. 3, where curves showing the relative change in molecular weight with depth of decomposition are presented for copolymers of MMA with MAA.

With the introduction into the chain of the PMMA homopolymer of 15% methacrylic acid units, the chain depolymerization process was suppressed to a considerable extent, the acts of destruction were mainly acts of bond rupture inside the polymer chain, and the length of the kinetic chain became very small. In this case, there was a sharp drop in the molecular weight curve, and the curve asymptotically approached zero with an increase in the depth of decomposition (Fig. 3, Curve 1). When the content of hetero units was small, the destruction process proceeded chiefly by a chain mechanism (Fig. 3, Curve 2), and the decrease in molecular weight took place considerably more slowly; the final molecular weight was 200,000 (a degree of polymerization of 200). Fragments of macromolecules of this size are decomposed completely as a result of a

single act of initiation (i.e., the kinetic chain length is ≈ 200), and there is no further decrease in the molecular weight.

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CONDENSATION OF THE SODIUM SALT OF THE ETHYL ESTER OF 1,3-INDANEDIONE-2-CARBOXYLIC ACID WITH DIAZOTIZED NITROANILINES

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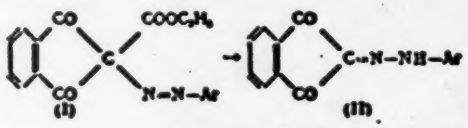
1,3-Indanedione readily reacts with aryldiazo compounds to form 2-arylhydrazones of indanetrione (triketohydrindene) [1-9], which are usually called 2-arylazoindanediones. The literature contains no data on the reaction of 1,3-indanedione derivatives with arylazo compounds.

When the interaction of arylazo compounds and esters of cyclohexanecarboxylic acids is carried out in a neutral or weakly acid medium, arylhydrazones of cyclanediones are formed [10-12]. In strongly basic media, the reaction proceeds with cleavage of the ring, and arylhydrazones of ketodicarboxylic acids are obtained in a solution of glacial acetic acid [12]. During a search for physiologically active substances, Henecka and co-workers reacted an ester of 2-piperidone-3-carboxylic acid with a p-methoxybenzenediazonium salt and obtained an intermediate azo compound [17].

We investigated the reaction products obtained from the condensation of diazotized o-, m-, and p-nitroanilines with the sodium salt of the ethyl ester of 1,3-indanedione-2-carboxylic acid. The reaction apparently proceeds with a shifting of the reactive center [18], and not by a Dimroth mechanism [19, 20].

By carrying out the reaction in an acid medium, we obtained yellow arylazo compounds (I), which were insoluble in water and readily soluble in methanol, ethanol, acetone, ether, glacial acetic acid, and dioxane. The corresponding 2-(nitrophenyl)hydrazono-1,3-indanediones (II) were formed by heating the alcoholic solutions



(I) (II)

a — Ar = p-$C_6H_4NO_2$,
b — Ar = o-$C_6H_4NO_2$,
c — Ar = m-$C_6H_4NO_2$.

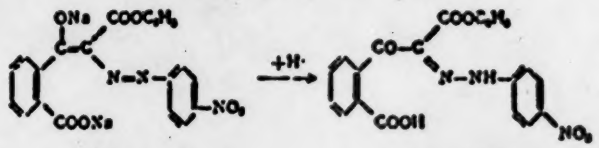
2-(Nitrophenyl)hydrazono-1,3-indanediones (II) were also obtained when the condensation reaction was carried out in an alkaline medium (pH ~ 8–9).

The ethyl ester of 2-(p-nitrophenyl)azo-1,3-indanedione-2-carboxylic acid (Ia) crystallized with one molecule of water from dilute ethanol, and gave a monooxime; 2-(p-nitrophenyl)hydrazono-1,3-indanedione (IIa) was formed when the alcoholic solution was refluxed.

The ethyl ester of 2-(p-nitrophenyl)azo-1,3-indanedione-2-carboxylic acid (Ia) dissolved in alkalies forming a red solution in which hydrolytic cleavage of the indanedione ring occurred with the formation of the sodium

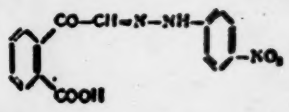
salt of the ethyl ester of o-carboxybenzoylglyoxalic acid p-nitrophenylhydrazone; when the solution was acidified, the acid itself was obtained as a yellow precipitate.

We were able to isolate the disodium salt (IV) of this acid by heating the azo ester (Ia) with sodium ethylate in ethanol; this product was red. The monoammonium, bis(dimethylamine), and dipiperidine salts of this acid were also prepared.



(IV) (III)

Acid (III) is stable toward hydrolysis, and it split out an ethoxy group only when refluxed for 5 hours in a mixture of acetic and sulfuric acids; this formed the p-nitrophenylhydrazone of o-carboxyphenylglyoxal (V):



(V)

Thus, we are the first to have obtained derivatives of cyclic β-diketones, undoubtedly pure azo compounds, while the previously described products of the condensation of β-diketones with aryldiazo compounds were either arylhydrazones of α-triketones or, more likely, tautomeric mixtures of the arylhydrazones of these triketones and arylazo compounds of β-diketones.

A further study of this reaction would permit clarification of the regularities involved in the formation of azo compounds of cyclic β-diketones, and would also clarify the possibility of using the latter compounds for the synthesis of a series of new compounds.

EXPERIMENTAL

Ethyl ester of 2-(p-nitrophenyl)azo-1,3-indanedione-2-carboxylic acid (Ia). A solution of 7.2 g (0.03 mole) of the sodium salt of the ethyl ester of 1,3-indanedione-2-carboxylic acid in 120 ml of water was added to diazotized p-nitroaniline (6 g, 0.043 mole), and the mixture was allowed to stand for 2 hours at a temperature of 0°. The product was recrystallized twice from ethanol, and 7 g (64%) of the ethyl ester of 2-(p-nitrophenyl)azo-1,3-indanedione-2-carboxylic acid (Ia) was obtained in the form of yellow plates. M. p. 155°.

$C_{18}H_{13}O_6N_3$. Found %: N 11.42
Calculated %: N 11.44

The hydrate of (Ia) was obtained in the form of yellow needles by recrystallization of (Ia) from dilute ethanol. M. p. 132°.

$C_{18}H_{13}O_6N_3 \cdot H_2O$. Found %: N 10.84; H_2O 4.70
Calculated %: N 10.90; H_2O 4.67

When the condensation was carried out in an alkaline medium at a pH of about 8-9, 2-(p-nitrophenyl)hydrazono-1,3-indanedione was obtained. M. p. 310 (Lit.: 311-313°) [9].

2-(p-Nitrophenyl)hydrazono-1,3-indanedione was also prepared by refluxing (Ia) in alcoholic solution. Carbon dioxide was eliminated from the carboethoxy group when (Ia) was refluxed with water. The ethanol remained in solution, as shown by iodoform test, and 2-(p-nitrophenyl)hydrazono-1,3-indanedione was precipitated. M. p. 310° (Lit.: 311-313°) [9].

(Ib) and (Ic) were prepared in a similar manner from the sodium salt of the ethyl ester of 1,3-indanedione-2-carboxylic acid and diazotized o- and m-nitroanilines. These were yellow crystalline substances which were recrystallizable from ethanol. M. p.s (Ib), 143°; (Ic), 129°.

	Found	(Ib) %:	N 11,62
		(Ic) %:	N 11,40
$C_{15}H_{11}O_5N_3$.	Calculated	(Ib) (Ic) %:	N 11,46

The oxime of the ethyl ester of 2-(nitrophenyl)azo-1,3-indanedione-2-carboxylic acid was prepared by refluxing for five hours an alcoholic solution of 0.73 g of (Ia) with 0.22 g of hydroxylamine hydrochloride and 0.12 g of sodium hydroxide. Yellow crystals of the oxime were obtained by recrystallizing the crude product from dioxane or ethanol. M. p. 207°.

	Found %	N 14,68
$C_{15}H_{12}O_5N_4$.	Calculated %	N 14,68

Hydrolytic cleavage of the ethyl ester of 2-(p-nitrophenyl)-azo-1,3-indanedione-2-carboxylic acid (Ia) with sodium ethylate. 10 g of azo ester (Ia) was refluxed for 3.5 hours in a solution of 1% sodium ethylate. The reaction mixture was then allowed to stand overnight. The red crystals of the disodium salt (IV) were dissolved in water, and the solution was acidified with hydrochloric acid. Recrystallization of the crude product from glacial acetic acid gave 8.5 g (80%) of yellow crystals of the p-nitrophenylhydrazone of the ethyl ester of o-carboxybenzoylglyoxalic acid (III).

	Found %	N 11,00
$C_{18}H_{15}O_7N_3$.	Calculated %	N 10,00

The disodium salt (IV) could not be recrystallized, since it hydrolyzed readily; therefore, the results of the analysis for nitrogen are somewhat low.

	Found %	N 9,23
$C_{18}H_{13}O_7N_3Na_2$.	Calculated %	N 9,79

Azo ester (Ia) is also hydrolytically cleaved with the formation of (III) by a solution of sodium hydroxide and even by a sodium bicarbonate solution.

p-Nitrophenylhydrazone of o-carboxyphenylglyoxal (V). 0.8 g of (III) was heated to boiling with 50 ml of glacial acetic acid and 50 ml of dilute sulfuric acid (1:1) for 5 hours. 0.2 g of soft brownish needles of the p-nitrophenylhydrazone of o-carboxyphenylglyoxal (V) was obtained. It was soluble in sodium bicarbonate solution. M. p. 225-226°.

	Found %	N 13,59
$C_{15}H_{11}O_5N_3$.	Calculated %	N 13,41

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THE SYNTHESIS OF SOME CARBON-SUBSTITUTED RHAMNOSES

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(Presented by Academician A. I. Oparin, June 18, 1959).

At the present time, the only known carbon-substituted derivatives of carbohydrates are those of glucose, xylose, mannose, arabinose, and galactose. As a result of syntheses carried out by the present authors, this series has been extended to derivatives of L-rhamnose, a carbohydrate which is widely distributed in nature. C-substituted rhamnoses were prepared by the interaction of α-chlortriacetylrhamnose with organomagnesium compounds. 1-Phenyl-1-desoxyrhamnose and its acetate, 1-p-tolyl-1-desoxy-2,3,4-triacetylrhamnose, and 1-allyl-1-desoxy-2,3,4-triacetylrhamnose were synthesized. The latter compound was subjected to further conversions, which resulted in the preparation of the dibromide and the mercurated derivative, the first organometallic compound in the sugar series.

The general type of these compounds is shown by the following structures

EXPERIMENTAL

L-rhamnose tetraacetate was prepared by acetylation of the carbohydrate with acetic anhydride in pyridine [1]. After acetylation, the reaction mixture was poured into water, and the product was extracted with chloroform; the chloroform solution was washed, dried over calcium chloride, and used for the preparation of chloroacetorhamnose without the separation of the syrup-like tetraacetate. The α-chloroacetorhamnose was prepared by the action of PCl_5 and $AlCl_3$ on the rhamnose tetraacetate in chloroform [2]. The yield of chloroacetorhamnose was 64% of theoretical.

1-α-Phenyl-1-desoxy-2,3,4-triacetylrhamnose. An ether solution of 5 g (0.016 mole) of chloroacetorhamnose was added dropwise over a period of 40 minutes to an ether solution of phenylmagnesium bromide prepared from 3.88 g (0.16 g-atom) of magnesium and 25.2 g (0.16 mole) of bromobenzene. The reaction mixture was stirred for 3 hours at room temperature, and was then heated with stirring for 5 hours. Upon completion of the reaction, water and acetic acid were added to the mixture, and the water layer was separated and evaporated to dryness. The dry residue was acetylated with acetic anhydride in the presence of sodium acetate. The acetylated product was extracted with ether. Evaporation of the ether yielded 2.75 g (48.4% of theoretical) of product in the form of a transparent syrup, which could not be crystallized.

The product was oxidized with alkaline permanganate, and benzoic acid was identified as an oxidation product. The substance was soluble in ether, methanol, and hot ethyl and isopropyl alcohols and insoluble in water and petroleum ether. The substance is described here for the first time.

Found %: C 61.38; H 6.54
$C_{13}H_{16}O_5$. Calculated %: C 61.71; H 6.38

1-α-Phenyl-1-desoxyrhamnose. 1 g of the phenylrhamnose triacetate described above was dissolved in 50 ml of absolute methanol, and the alcoholic solution was saturated with ammonia (3 g increase in weight) and allowed to stand overnight. The methanol was then evaporated, and the residue was washed with warm ether to remove the acetamide and recrystallized from methyl acetate. 0.54 g (84% of theoretical) of a light, transparent syrup was obtained, and this was converted by prolonged storage in a vacuum desiccator over phosphorus pentoxide to a caramel-like, viscous product. Oxidation of this product gave benzoic acid. The substance was soluble in water, methanol, and pyridine and insoluble in ether and petroleum ether.

The substance is described here for the first time.

Found %: C 63.93; H 7.33
$C_{13}H_{18}O_4$. Calculated %: C 64.48; H 7.14

1-p-Toyl-1-desoxy-2,3,4-triacetylrhamnose. To 3.88 g (0.16 g-atom) of magnesium was added an ether solution of 27.36 g (0.16 mole) of p-bromotoluene, and to the resulting solution was added dropwise and with stirring an ether solution of 5 g (0.016 mole) of chloroacetorhamnose. Further treatment was carried out as in the case of phenylacetorhamnose.

There was obtained 1.74 g (30% of theoretical) of a light syrup, which yielded terephthalic acid when oxidized. The substance was soluble in ether and methanol and insoluble in water and petroleum ether. The substance is described here for the first time.

Found %: C 62.31; H 6.88
$C_{19}H_{24}O_7$. Calculated %: C 62.63; H 6.59

1-Allyl-1-desoxy-2,3,4-triacetylrhamnose. To a solution of 5 g (0.016 mole) of chloroacetorhamnose in 70 ml of absolute ether was added 24.4 g (0.21 mole) of allyl bromide in 60 ml of absolute ether. Half of the resulting mixture was added to 5.1 g (0.21 g-atom) of magnesium turnings. The second half was added dropwise with stirring. The reaction mixture was stirred for 2 hours at room temperature and then for 5 hours while being heated on a water bath. Upon completion of the reaction, the mixture was decomposed with water and dilute acetic acid, and the aqueous layer was separated and evaporated to dryness under water-aspirator vacuum. The dry residue was acetylated with acetic anhydride in 10 ml of pyridine. The acetylated product was extracted with ether and the ether extract was washed with a dilute solution of H_2SO_4, water, and a saturated solution of sodium bicarbonate, and dried over calcium chloride.

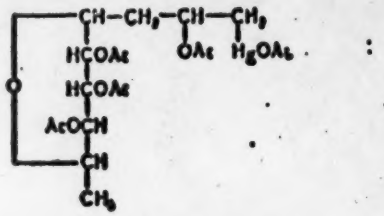
There was obtained 2.3 g (45% of theoretical) of a syrup from which we were able to isolate 0.61 g of a crystalline product with an m. p. of 59-60°. The substance is described here for the first time.

Found %: C 56.55; H 7.22
$C_{15}H_{22}O_7$. Calculated %: C 57.32; H 7.00

1-Dibromoallyl-1-desoxy-2,3,4-triacetylrhamnose. 0.6 g of the allylacetorhamnose described above was dissolved in 8 ml of acetic acid; 0.15 ml of bromine was added to the solution, and the mixture was allowed to stand for 1 hour. The mixture was then poured into water, and the product was extracted with ether; the ether extract was washed with soda solution and water and dried over sodium sulfate. There was obtained 0.68 g (75% of theoretical) of a semi-liquid product from which was isolated 0.22 g of crystalline isomer with an m. p. of 143-144°. The substance was soluble in alcohol and ether and insoluble in water and petroleum ether. 34.31% Br was found by analysis with calcium oxide (Br calculated, 33.7%). The substance is described here for the first time.

Mercury derivative of allylacetorhamnose. 1.4 g of allylacetorhamnose was dissolved in 8 ml of acetic acid, and to the solution was added a solution of 1.5 g of mercuric acetate in 15 ml of acetic acid [4]. The mixture was heated at 65-75° on a water bath 2.5 hours; the solution was then poured into water, and the precipitate was filtered, washed with ether, and dried over phosphorus pentoxide. A crystalline ma-

terial was obtained which did not melt when heated to 300°. Analysis of the product for mercury by the thiocyanate method showed 34.93% Hg (Hg calculated, 31.26%). This corresponds to the formula:



A 12-hour treatment of an aqueous acetic acid solution of the substance with a saturated solution of sodium chloride gave the insoluble chloromercuric derivative of allylacetorhamnose. Analysis for chlorine gave 4.99% (calculated, 5.14%). The substance is described here for the first time.

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ON THE CONCURRENT FORMATION OF FIVE- AND SIX-MEMBERED RINGS FROM PARAFFINS (C_5- AND C_6-DEHYDROCYCLIZATION) OVER PLATINIZED CARBON

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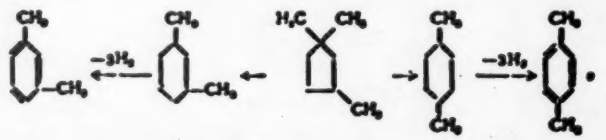
In 1936, P. A. Kazanskii and A. F. Plate showed that, at 300° and over platinized carbon, paraffinic hydrocarbons undergo dehydrocyclization with the formation of aromatic hydrocarbons [1]. Judging from the structure of these aromatics, they must have been formed by direct closure of the open hydrocarbon chain to a six-membered ring without any intermediate chain isomerization [2].

It was later shown that in the presence of platinum, the paraffin is first converted to the corresponding cyclohexane hydrocarbon, which is then converted to an aromatic by subsequent dehydrogenation [3, 4].

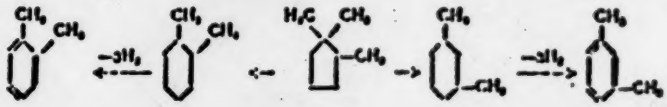
In 1954, it was established that during the dehydrogenation of n-heptane and n-octane under the conditions indicated above, in addition to aromatic hydrocarbons, the corresponding cyclopentane homologs are also formed; in this process, the yield of cyclopentanes even exceeded the yield of aromatic hydrocarbons [5, 6]. The formation of cyclopentane hydrocarbons occurred to a particularly appreciable extent when the feed consisted of those branched paraffins which contain five carbon atoms in their main chain, for example, isooctane (2,2,4-trimethylpentane) and 3-ethylpentane [7-9]. However, in this case, aromatic hydrocarbons are formed along with the cyclopentanes. The mechanism by which the aromatics are formed must be complex; specifically, there must either take place preliminary isomerization of the paraffin with the formation of a longer chain, which can then be closed directly to a six-membered ring, or the aromatic hydrocarbons must be formed from cyclopentanes. The first hypothesis is improbable, since the isomerized paraffins should yield the cyclopentane homologs of corresponding structure, and this is not observed. The second hypothesis has been confirmed by experiment, as will be shown below.

Actually, the product from isooctane contains only one cyclopentane hydrocarbon [8] – 1,1,3-trimethylcyclopentane – and three aromatics – m-xylene, p-xylene, and toluene – (the three latter compounds in relative amounts of 62, 34, and 4% respectively). At present, the formation of m- and p-xylenes from 1,1,3-trimethylcyclopentane is easily represented by the following scheme:



in which the five-membered ring is expanded at the expense of one of the gem-methyl groups. Ring expansion at the expense of the lone methyl group must be subordinate since in this case, the formation of 1,1-dimethylcyclohexane would be expected, and this, under the conditions of the reaction, would yield chiefly toluene, significantly less o-xylene, still less m-xylene (in a ratio of 25 : 5 : 1), and no p-xylene at all [10].

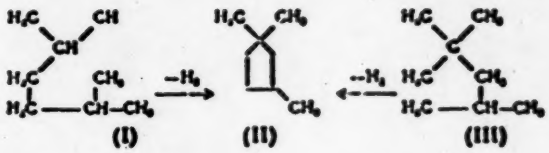
The hypothesis that aromatics are formed by expansion of a five-membered ring is confirmed by the fact that when 2,2,3-trimethylpentane was contacted with platinized carbon under the same conditions as in the case of isooctane, the resulting aromatic hydrocarbons comprised 66% m-xylene and 26% o-xylene; p-xylene was almost completely absent. This can be readily understood if it is recalled that 2,2,3-trimethylpentane forms 1,1,2-trimethylcyclopentane [11], the five-membered ring of which can expand with the formation of o- and m-xylenes according to



It must be pointed out that there is no specific proof in the literature of the possibility of expansion of a five-membered hydrocarbon ring when such simple systems are contacted with platinized carbon under such mild conditions (300-310°, space rate 0.2 hours^{-1}) as in the cases enumerated above, although such expansion would be expected [1]. Similar conversions have been noted only for more complex polynuclear systems having at least one benzene ring. Moreover, it has even been reported that 1,1-dialkylcyclopentanes remain unchanged under similar conditions in the absence of a carrier gas, and react with expansion of the ring only in a stream of hydrogen [12].

Therefore, we undertook a direct experiment with 1,1,3-trimethylcyclopentane in the absence of a carrier gas; this experiment showed that ring expansion actually does take place with the formation of the same aromatic hydrocarbons as are formed from isooctane, though in a somewhat different ratio (m-xylene/p-xylene = 1 : 1). We previously observed the formation of a very small amount of aromatics from n-propylcyclopentane [6]. In the present work, parallel experiments were carried out with 1,1,3-trimethylcyclopentane and n-propylcyclopentane under the same conditions, and these experiments showed that considerably more aromatics are obtained from the first hydrocarbon than from the second. This is in agreement with the above statement regarding the predominance of ring expansion at the expense of gem-methyl groups.

From the above discussion, the question arises as to whether aromatic hydrocarbons formed from paraffins containing six or more carbon atoms in a straight chain are not formed through intermediate products having a five-membered ring. Such a



(I) (II) (III)

proposal has appeared in the literature, although it was not experimentally proved [13, 14]. Since it was not possible at the time of the present investigation to study the behavior in this regard of paraffins having a large number of carbon atoms, we turned to 2,5-dimethylhexane (I), the aromatization of which was previously studied by us in some detail [1, 3]. If in this case aromatization proceeds through an intermediate stage in which a cyclopentane hydrocarbon is formed, the primary product should be the same as that formed from isooctane (III), 1,1,3-trimethylcyclopentane (II), and consequently, the composition of the aromatics obtained from 2,5-dimethylhexane and isooctane should be closely similar or identical. If 2,5-dimethylhexane closes directly to a six-membered ring, the sole aromatization product should be p-xylene, and m-xylene should be absent. It is natural that 2,5-dimethylhexane, like other paraffins, should undergo some dehydrocyclization with the formation of a five-membered ring, and, therefore, a certain amount of aromatic hydrocarbons could be formed from the resulting 1,1,3-trimethylcyclopentane independently of other routes of formation. Consequently, the presence of m-xylene in the cyclization products is quite probable, but its fraction in the product mixture should depend on whether the direct formation of a six-membered ring is possible.

The experiment showed that the aromatics formed from 2,5-dimethylhexane consist of 95% p-xylene and only 5% m-xylene. The constants of the catalyzate after the removal of the aromatics were considerably higher,

which suggests the presence of about 5% 1,1,3-trimethylcyclopentane. Thus, in the case of 2,5-dimethylhexane, a large part of the aromatics was formed by the direct closure of the paraffin chain to a six-membered ring, and not through the intermediate formation of a cyclopentane hydrocarbon. Consequently, the assumption that this stage is required in the formation of aromatic hydrocarbons from paraffins of any chain length is incorrect. This give us the right to assume that, under the conditions used in the present work, two independent paraffin cyclization reactions can occur concurrently: one resulting in the formation of a five-membered ring, which we propose to call C_5-dehydrocyclization, and one resulting in the formation of a six-membered ring, i.e., C_6-dehydrocyclization. We shall use these terms in our future communications.

EXPERIMENTAL

The original hydrocarbons were carefully purified by distillation in columns having an efficiency of 100 theoretical plates and by chromatography. Their constants were in good agreement with the literature values [15].

The catalyst used in all experiments, except the experiments with n-propylcyclopentane, was freshly prepared platinized carbon (20% Pt). It was prepared by the method due to Zelinskii [16] by reduction of H_2PtCl_6 with formaldehyde in an alkaline medium. The experiments were carried out in a glass tube at 310°. The hydrocarbons investigated were passed over the catalyst at a space rate of 0.2 hours^{-1} without a carrier gas. The catalyzate was collected, weighed, and its constants were determined, after which it was chromatographed on silica gel. One fraction was collected until aromatics or unsaturates appeared in the eluate, and another 1 or 2 fractions were collected until the hydrocarbons had been displaced from the adsorbent. The olefin content of the catalyzate was determined by bromine number, the aromatics were determined from the difference in refractive index before and after chromatographing, and the cyclopentanes were determined from the difference in refractive index of the chromatographed catalyzate and that of the original hydrocarbon. The aromatic fractions were washed free of a small amount of alcohol which had been used as a displacing liquid during the chromatographic separation, and were investigated by Raman spectroscopy*.

Aromatic hydrocarbons from isooctane. 95.1 g of isooctane (b. p. 99.2°/760 mm, n_D^{20} 1.3915, d_4^{20} 0.6919) was passed over 60 ml of catalyst. The catalyzate (93.4 g, 98.2% yield, n_D^{20} 1.3984) contained about 4% aromatics, 3% olefins, and 13.5% 1,1,3-trimethylcyclopentane. Chromatographing of the catalyzate yielded Fraction I (n_D^{20} 1.3942) and Fraction II (3.7 g, n_D^{20} 1.4858, d_4^{20} 0.8452). Spectroscopic analysis of Fraction II showed that the aromatics present consisted of 62% m-xylene, 34% p-xylene, 4% toluene, and traces of o-xylene.

Aromatic hydrocarbons from 2,2,3-trimethylpentane. 129.4 g of 2,2,3-trimethylpentane (b. p. 109.8°/760 mm, n_D^{20} 1.4030, d_4^{20} 0.7160) was passed over 100 ml of catalyst. The catalyzate (128.0 g 98.9% yield, n_D^{20} 1.4068) contained 2.5% aromatic hydrocarbons, 4.5% olefins, and 5% 1,1,2-trimethylcyclopentane. Chromatographing of this catalyzate yielded Fraction I (n_D^{20} 1.4041) and Fraction II (4.1 g, n_D^{20} 1.4660, d_4^{20} 0.8123). Spectroscopic analysis of Fraction II showed that the aromatic hydrocarbons present consisted of 68% m-xylene, 26% o-xylene, 6% toluene, and traces of p-xylene.

Aromatic hydrocarbons from 2,5-dimethylhexane. 29.3 g of 2,5-dimethylhexane (b. p. 109.3°/760 mm, n_D^{20} 1.3925, d_4^{20} 0.6935) was passed over 30 ml of catalyst. The catalyzate (27.4 g, 93.5% yield, n_D^{20} 1.4010, d_4^{20} 0.7065) contained 8% aromatic hydrocarbons, 1.5% olefins, and, judging from the constants of the chromatographed catalyzate, 5% 1,1,3-trimethylcyclopentane. 27.0 g of this catalyzate was chromatographed to yield Fraction I (23.8 g, n_D^{20} 1.3935, d_4^{20} 0.6950) and Fraction II (2.4 g, n_D^{20} 1.4779 d_4^{20} 0.8319). Spectroscopic analysis of Fraction II showed that the aromatics present consisted of 95% p-xylene and 5% m-xylene. It was not possible to obtain positive spectroscopic proof of the presence of 1,1,3-trimethylcyclopentane in Fraction I, since the lines corresponding to this hydrocarbon were weak.

Expansion of the five-membered ring of 1,1,3-trimethylcyclopentane. 13.6 g of 1,1,3-trimethylcyclopentane (b. p. 104.9°/760 mm, n_D^{20} 1.4112 d_4^{20} 0.7483) was passed over 10 ml of catalyst. The catalyzate (13.4 g, 98.5% yield, n_D^{20} 1.4172) contained 9% aromatics and 4% olefins. Chromatographing of this catalyzate yielded Fraction I (10.0 g n_D^{20} 1.4095, d_4^{20} 0.7442), Fraction II (1.1 g, n_D^{20} 1.4103) and Fraction III (1.0 g, n_D^{20} 1.4807, d_4^{20} 0.8405). Spectroscopic analysis of Fraction III showed that the aromatics present consisted of 50% m-xylene and 50% p-xylene.

*All spectroscopic investigations reported in the present paper were carried out by V. T. Aleksanyan and Kh. E. Sterin, science students at the Commission of Spectroscopy, Academy of Sciences, USSR; we express our deep appreciation for their aid in this work.

Effect of the presence of gem-methyl groups on the ease of expansion of the five-membered ring. The experiments were carried out using a stabilized catalyst, since the change in activity from experiment to experiment when freshly prepared catalyst was used would not permit comparison of two different hydrocarbons with one portion of catalyst. Therefore, isooctane was passed over 10 ml of catalyst under the usual experimental conditions until the catalyst activity became constant (12.5% cyclization of the isooctane). The isooctane was then flushed from the catalyst with n-pentane and then with hydrogen. 6.2 g portions of 1,1,3-trimethylcyclopentane and n-propylcyclopentane (b. p. 130.9°/760 mm, n_D^{20} 1.4263, d_4^{20} 0.7763) were then passed in turn over the catalyst; in the interval between the two feeds, the residual hydrocarbon was flushed from the catalyst with n-pentane and hydrogen. The catalyzates, which were obtained with yields of 88.6-88.7%, had the following properties; the catalyzate from 1,1,3-trimethylcyclopentane n_D^{20} 1.4160, d_4^{20} 0.7527, after chromatographing had n_D^{20} 1.4101 and consequently, contained 7% aromatics; the catalyzate from n-propylcyclopentane n_D^{20} 1.4260, d_4^{20} 0.7744 and after chromatographing had n_D^{20} 1.4254 i.e., it contained not more than 1% aromatic hydrocarbons.

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CHLORINATION OF MONOCHLOROPROPANES

B. A. Krentsel', Academician A. V. Topchiev, and D. E. Il'ina

In considering the effect of the structure of paraffinic hydrocarbons on the course of hydrocarbon chlorination, the order of replacement of hydrogen atoms by chlorine during the chlorination of monochloro derivatives to dichloro derivatives is of substantial interest. The many investigators studying this problem have taken different points of view. In papers by Hass and McBee [1, 2] it was asserted that a chlorine atom attached to a carbon atom hindered further addition of chlorine to that carbon atom during vapor-phase chlorination. However, this position is incorrect. In particular, it is not in agreement with the earlier statements of Regnault [3] and Staves [4], who asserted that during the chlorination of monochloro derivatives of paraffinic hydrocarbons, the second chlorine atom replaces a hydrogen attached to the same carbon atom as the first chlorine. On the other hand, Mayer [5], studying the chlorination of organic compounds, pointed out that the second chlorine atom replaces a hydrogen at a carbon adjacent a carbon already attached to a chlorine. Similar results were obtained by Herzfelder [6], who also studied the chlorination of hydrocarbons by antimony pentachloride. However, he also noted that in many cases, 1,1-dichloro derivatives are obtained.

Muskat and Northrup [7] found that during the photochemical chlorination of monochlorobutane in the vapor phase, all possible dichloro derivatives are formed including 16% 1,1-dichloro-, 23% 1,2-dichloro-, 26% 1,3-dichloro-, and 7.4% 1,4-dichlorobutane.

Vaughan and Rust [8] showed that the temperature at which the chlorination is carried out has a specific effect on the ratios of isomeric dichlorides. Thus, during thermal chlorination of ethyl chloride there was an increase in the yield of 1,1-dichloroethane (as compared to the amount of 1,2-dichloroethane formed) with an increase in temperature. It is curious that these same authors observed the formation of significant amounts of

TABLE 1

Thermal Chlorination of Chloropropanes

Expt. No.	Chloride charged	Amount of Cl charged, g	Temp., °C	Wt. of product, g	Prod. compn., wt., % (from distn. data)			Dichloride compn., wt. % of total dichlorides			
					monochlorides	dichlorides	higher chlorides	2,2-dichloropropane	1,1-dichloropropane	1,2-dichloropropane	1,3-dichloropropane
22	1-chloropropane	47	305	69,9	25,2	49,0	25,8	—	25,9	43,7	30,4
23	1-chloropropane	34	342	46,8	20,9	45,2	33,9	—	23,2	39,8	37,0
20	2-chloropropane	41	300	46,6	18,9	41,0	40,1	54,8	—	45,2	—
24	2-chloropropane	33	302	45,3	15,3	66,7	18,0	60,2	—	39,8	—
26	2-chloropropane	17	302	21,3	14,1	65,8	20,1	47,4	—	52,6	—
25	2-chloropropane	40	342	53,8	21,3	62,0	16,7	61,1	—	38,9	—

1,1,1-trichloroethane during the further chlorination of 1,1-dichloroethane (in a mixture with 1,2-dichloroethane).

Thus contrary to the rule of McBee and Hass, the formation not only of 1,1-dichloro derivatives, but also of 1,1,1-trichloro derivatives is possible.

In delineating the phenomenon of the vinyl effect during the chlorination of hydrocarbons, Tishchenko and Churbakov (9) were also led to the conclusion that the formation of 1,1-substituted derivatives is possible during the chlorination of monochloro derivatives.

EXPERIMENTAL

The present paper describes an experimental study of the chlorination of isomeric monochloropropanes, which were priorly prepared by thermal chlorination of propane.

In the first series of experiments, thermal chlorination of monochloropropanes was carried out in an apparatus similar to that used for the thermal chlorination of propane [10]. The chlorination was carried out at temperatures of 300-340° and at a ratio of chloride to chlorine of 1:1 (by volume).

The reaction products which condensed in the receiving system, after appropriate careful treatment (washing, drying, etc.), were subjected to precise distillation in a fractionation column (20 theoretical plates), and the resulting fractions were characterized by their physicochemical properties. In addition, the following dichloropropanes were identified by chemical means in the various fractions: 1,3-dichloropropane, identified through the corresponding propanediol obtained by hydrolysis with aqueous potassium carbonate by a method described in the literature, and 1,2- and 2,2-dichloropropanes, identified by their condensation products with benzene. 1,1-Dichloropropane was identified from its physicochemical properties. The results of the experiments on the thermal chlorination of isomeric chloropropanes are presented in Table 1.

TABLE 2

Physicochemical Properties of the Dichloropropanes

	2,2-Dichloropropane		1,1-Dichloropropane		1,2-Dichloropropane		1,3-Dichloropropane	
	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}
Experimental data	1,4127	1,0905	1,4292	1,1325	1,4300	1,1548	1,4510	1,1981
Literature data	1,4117	1,0915	1,4283	1,1321	1,4383	1,1545	1,4520	1,1986

The methods used for the distillation and separation of the various dichloropropane fractions guaranteed that products of a sufficiently high degree of purity would be obtained; that such was the case is shown by the data of Table 2.

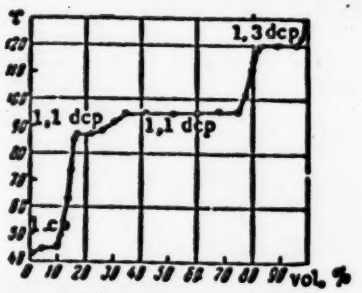

Fig. 1. Distillation curves of the dichloropropanes produced by photochemical chlorination of 1-chloropropane (cp – chloropropane, dcp – dichloropropane).

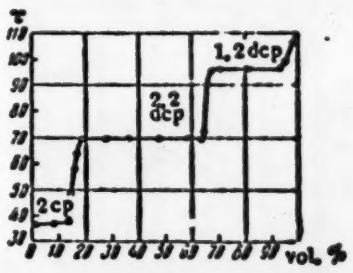

Fig. 2. Distillation curves of the dichloropropanes produced by photochemical chlorination of 2-chloropropane (cp – chloropropane, dcp – dichloropropane).

As shown by the experimental data presented before only 1,1-, 1,2-, and 1,3-dichloropropanes were formed by the thermal interaction of 1-chloropropane with chlorine. 2,2-Dichloropropane was not formed, which indicates the absence of pyrolysis under the conditions of the experiments. A considerable amount of 2,2-dichloropropane and somewhat less of the 1,2-dichloro compound were formed during thermal chlorination of 2-chloropropane. These data once again confirm the formation of α,α'-derivatives during chlorination of chloroalkanes.

The observations made during the photochemical chlorination of chloropropanes were very interesting.

The photochemical chlorination was carried out in a manner designed to avoid the formation of tri- and polychlorides; the chlorine was passed into the reaction mixture in an amount of 50-80% of that theoretically required for the formation of dichloro derivatives. The resulting reaction products were treated and identified

TABLE 3

Photochemical Chlorination of Monochloropropanes

Expt. no.	Wt. of chloride charged, g	Cl charged, % of theor. for dichloropropane	Prod. obtained, g	Prod. compn., wt. % (of total dichlorides			Dichloropropane compn., wt. % (of total dichlorides)			
				monochloropropane	dichloropropanes	higher chloropropanes	2,2-dichloropropane	1,1-dichloropropane	1,2-dichloropropane	1,3-dichloropropane
1-Chloropropane										
168	120	78	165,6	12,1	69,2	18,7	—	15,2	61,0	23,8
170	116	68	155,7	17,0	63,5	19,5	—	22,4	49,6	28,0
173	130	65	182,0	20,8	61,8	17,4	—	24,8	51,5	23,7
182	117	53	140,0	33,9	55,1	11,0	—	15,5	59,3	25,2
194	117	57	154,0	25,9	57,5	16,6	—	14,0	55,4	30,6
17	117	72	152,6	17,7	65,6	16,7	—	9,0	63,3	27,7
2-Chloropropane										
169	114	72	154,2	18,1	73,8	10,1	57,5	—	42,5	—
171	111	79	188,1	9,0	83,5	7,5	57,0	—	43,0	—
183	114	51	138,0	32,2	57,2	10,6	58,0	—	42,0	—
187	114	60	145,0	26,6	54,4	19,0	58,8	—	41,2	—
191	114	58	136,0	27,7	55,7	16,6	58,5	—	41,5	—
118	113	66	145,0	20,7	64,0	15,3	54,1	—	45,9	—

in the manner described above for the thermal chlorination products. The results of the experiments on the photochemical chlorination of chloropropanes are presented in Table 3. Distillation curves of the dichlorides obtained are presented in Figures 1 and 2.

The average isomer composition of the resulting dichloropropanes is characterized by the data presented in Table 4.

TABLE 4

Average Composition of Dichloropropanes

Original monochloropropane	Average content in chlorination products, %			
	1,1-dichloropropane	1,2-dichloropropane	1,3-dichloropropane	2,2-dichloropropane
1-Chloropropane	15	59	26	—
2-Chloropropane	—	43	—	57

Thus, the position of the chlorine atom in a chloroalkane molecule has a substantial effect on the order of succeeding replacement of hydrogen by chlorine.

In the case of 2-chloropropane, the major amount of the chlorine replaces hydrogen at the carbon atom already attached to a chlorine, and 2,2-dichloropropane is formed in predominant amount. In the chlorination of 1-chloropropane, replacement of hydrogen by chlorine preferentially proceeds so that 1,2-dichloropropane is formed. This fact is explained by the difference in the electronic structures of the isomeric alkyl chlorides.

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APPLICATION OF THE HAMMETT EQUATION TO ISOTOPIC HYDROGEN-EXCHANGE REACTIONS

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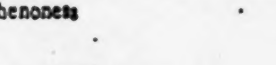
The present work was devoted to an investigation of the effect of substituents on the mobility of hydrogen of the methyl group of para-substituted acetophenones



The best method of studying the mobility of hydrogen atoms is by isotopic hydrogen exchange.

An advantage of the isotopic exchange method is that the initial and final substances are chemically identical. The reaction medium remains unchanged throughout the entire reaction.

From this same point of view, a second advantage of the hydrogen-exchange method is that the size of the substituent (deuterium) is very small; hence steric factors cannot be determinative in this reaction.

As is well known, the Hammett equation [1] establishes a quantitative relationship between the reactivity of compounds of the benzene series and the nature of substituents in the para or meta position.

$$\log \frac{K}{K_0} = \sigma\rho,$$

where K is the reaction rate (or equilibrium) constant of the substituted compound, K_0 is the reaction rate (or equilibrium) constant of the unsubstituted compound, σ is the substituent constant and depends only on the nature of the substituent and its position in the benzene ring, and ρ is a constant for the specific reaction and determines the sensitivity of the reaction to the effect of the substituent.

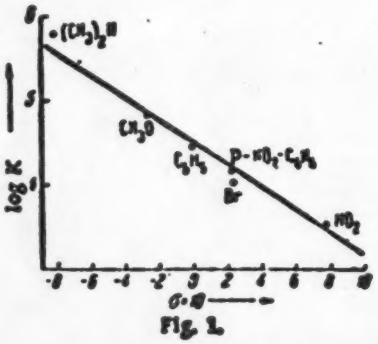


Fig. 1.

However, although the applicability of Hammett's equation has been investigated for many reactions [2], up to the present time this equation has not been applied to isotopic hydrogen-exchange reactions. We have studied the applicability of the Hammett equation to hydrogen-exchange reactions of para substituted acetophenones in alkaline medium.

The hydrogen exchange reactions were carried out in a medium of absolute deuteriethanol used in considerable excess, under the influence of sodium ethylate as a catalyst. The first order reaction rate constants were determined at 20° for hydrogen-deuterium exchange of acetophenone and some of its para-substituted derivatives, nitro-, bromo-, dimethylamino-, and methoxy-acetophenones, and of p-acetylbiphenyl and 4-nitro-4'-acetylbiphenyl, which were considered as derivatives of acetophenone (see Table 1).

TABLE 1

Ketone	Melting point, °C		$K_{1\varphi}$, sec.$^{-1}$	Substituent in para position of acetophenone	σ para*
	initial ketone	ketone recovered			
Acetophenone	(b. p. 78.5°/10mm)		$(3.62 \pm 0.25) \cdot 10^{-5}$	–	0
p-Nitroacetophenone	79.7–80.1	79.2-79.7	$(3.04 \pm 0.09) \cdot 10^{-4}$	NO_2	0.778
p-Bromoacetophenone	52.5-53.0	52.5-53.0	$(9.80 \pm 1.15) \cdot 10^{-5}$	Br	0.23
p-Methoxyacetophenone	37.8-38.5	37.2-37.4	$(1.39 \pm 0.16) \cdot 10^{-5}$	CH_3O	−0.268
p-Dimethylaminoacetophenone	105.2-105.7	105.7-106.4	$(1.62 \pm 0.17) \cdot 10^{-6}$	$(CH_3)_2N$	−0.83
p-Acetylbiphenyl	122.0-122.5	122.0-122.5	$(3.62 \pm 0.26) \cdot 10^{-5}$	C_6H_5	−0.01
4-Nitro-4'-acetylbiphenyl	153.4-153.9	153.0-154.1	$(6.69 \pm 0.57) \cdot 10^{-5}$	$n\text{-}NO_2\text{-}C_6H_4$	0.223

* The values of σ para were taken from the tables of McDaniel and Brown [3] except for the value of σ for $p\text{-}NO_2\text{-}C_6H_4$ which was taken from the paper by Berliner [4].

A graph was plotted showing the dependence of the logarithm of the reaction rate constant for hydrogen exchange of the substituted acetophenones on the substituent constant σ, for the para position. As seen from Fig. 1, this dependence is linear.

It has thus been shown that the Hammett equation is obeyed for hydrogen exchange reactions of substituted acetophenones in an alkaline medium. The value of ρ found for this reaction is 1.43. The correlation coefficient, r, is 0.99.

EXPERIMENTAL

The hydrogen exchange reaction was carried out in a medium of absolute deuterioethanol (with a deuterium content in the hydroxyl of 8-9 atom %), which acted as the solvent and deuterium donor. The deuterioethanol was used in considerable excess, 1 mole of ketone for 200-800 moles of deuterated alcohol, depending on the solubility of the ketone. Using acetophenone, it was shown that under these conditions, the first order reaction rate constant for the hydrogen exchange does not change when the amount of deuterated alcohol used is changed by a factor of 4.

Special experiments showed that hydrogen exchange does not occur between ketones and deuterated alcohol in the absence of a catalyst. A solution of sodium ethylate in deuterioethanol was used as the catalyst. In the determination of catalyst concentration, the sodium ethylate was neutralized with an excess of potassium biiodate, $KIO_3 \cdot HIO_3$, used as a monobasic acid, and the excess biiodate was determined iodometrically.

The hydrogen exchange reaction was carried out by adding to the solution of ketone in deuterioethanol a solution of catalyst in an amount such that the total concentration of sodium ethylate in the reaction solution was 0.00036 N. The time at which reaction began was taken as the time at which the catalyst was added.

Samples were collected by forcing part of the solution from the reaction flask with dry nitrogen. The hydrogen exchange reaction was stopped either by cooling to −80° or by dilution with water (25-fold).

The reaction was stopped by cooling to −80° when the ketone was p-nitroacetophenone, 4-nitro-4'-acetylbiphenyl, p-dimethylaminoacetophenone, or p-acetylbiphenyl. In this case, the ketones precipitated. In the case of acetophenone, p-bromoacetophenone, and p-methoxyacetophenone, the reaction was stopped by dilution.

Control experiments showed that either cooling to −80° or 25-fold dilution with water effectively stopped the hydrogen-exchange reaction.

Determination of the deuterium content was carried out by the falling drop method. The reaction rate constants presented in Table 1 are root-mean-square averages of 8-10 measurements.

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THE REARRANGEMENT OF ESTERS OF α-HYDROXYALKANEPHOSPHONIC ACIDS TO THE ISOMERIC PHOSPHATES.

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(Presented by Academician B. A. Arbuzov, June 12, 1959)

Alkaline dehydrochlorination of esters of α-hydroxy-β-haloalkanephosphonic acids yields both the normal products – esters of epoxyalkanephosphonic acids – as shown by B. A. Arbuzov and co-workers [1] and by V. S. Abramov and A. S. Kapustina [2], and also rearrangement products – unsaturated esters of phosphoric acid [3, 4].

$$(RO)_2P(O)-CH(OH)-CX_2 \xrightarrow{NaOH} (RO)_2P(O)-O-CH=CX_2.$$

According to Pengelsdorf [5], such a rearrangement can take place only if X is capable of elimination as an anion. In other cases, decomposition to an aldehyde and a dialkyl phosphite proceeds under the influence of an alkali [6].

A similar rearrangement is brought about by the action of sodium cyanide on bisulfite compounds of esters of α-ketophosphonic acids [7]. In place of the expected α-hydroxy-α-cyanoalkanephosphonates, the isomeric phosphates are obtained:

$$(RO)_2P(O)-C(O^-)(CN)-R' \rightarrow (RO)_2P(O)-O-C^-(CN)-R' \xrightarrow{H^+} (RO)_2P(O)-O-CH(CN)-R'.$$

One of us has studied the reaction involved in the direct action of dialkyl phosphites on biacetyl [3]; a reaction occurs when the reactants are heated to 100° in a sealed tube, and it leads to esters of α-hydroxy-α-acetoethanephosphonic acid. A repitition of the experiments under the same conditions led to the same esters of α-hydroxy-α-acetoethanephosphonic acid; these esters are shown in Table 1 (Products A).

When the experiments were carried out under different conditions, products having different physical constants were obtained. This impelled us to undertake a detailed study of the effect of experimental conditions on the course of the reaction between dialkyl phosphites and biacetyl, including a study of the structures of the resulting products. It was found that if the reaction between dialkyl phosphites and biacetyl is carried out in a flask at temperatures above 100°, Products B of Table 1 are obtained. The effect of experimental conditions on the course of the reaction was studied in greatest detail for the reaction of diethyl phosphite with biacetyl, as shown in Table 2.

An investigation of Product A resulting from the reaction of diethyl phosphite with biacetyl showed that a hydroxyl group was present; the hydroxyl content was found to be 8.16% (calculated, 8.04%) by Tserevitinov's

TABLE 1

Formula of compound	B. p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield, %	Content P, % found	Content P, % calc.
$(CH_3O)_2P(O)-C(CH_3)(OH)-CO-CH_3$ A	110°/4	1,4530	1,2391	42,70	42,31	51,0	15,80	15,81
$(CH_3O)_2P(O)-O-CH(CH_3)-CO-CH_3$ B	132–133°/15	1,4340	1,2210	41,84	41,91	58,7	15,77	15,81
$(C_2H_5O)_2P(O)-C(CH_3)(OH)-CO-CH_3$ A	138–140°/10	1,4445	1,1307	52,20	51,55	66,6	13,87	13,84
$(C_2H_5O)_2P(O)-O-CH(CH_3)-CO-CH_3$ B	133–134°/10	1,4230	1,1148	51,17	51,15	62,1	13,93	13,84
$(C_3H_7O)_2P(O)-C(CH_3)(OH)-CO-CH_3$ A	142°/4	1,4490	1,0641	70,44	70,02	84,0	11,11	11,07
$(C_3H_7O)_2P(O)-O-CH(CH_3)-CO-CH_3$ B	160–161°/10	1,4270	1,0178	70,55	69,62	33,1	11,26	11,07

TABLE 2

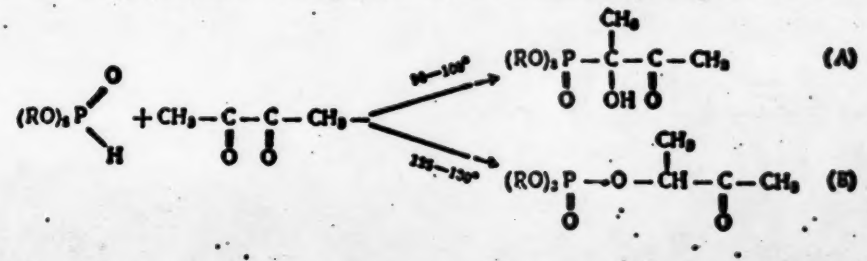
Effect of Experimental Conditions on the Course of the Reaction of Diethyl Phosphite with Biacetyl

Experimental conditions	Reaction temp., °C	Time, hours	Product obtained	Yield, %
Heating in sealed tube	90-100	9-10	A	66.6
Heating in sealed tube in presence of moist benzene	90-100	9-10	A	65.4
Heating in flask with reflux condenser	90-100	4	A	32.1
Heating under nitrogen in flask with reflux condenser	90-100	5	A	51.5
Heating in flask with reflux condenser	125-130	3-7	B	62.1
Heating under nitrogen in flask with reflux condenser	125-130	6-7	B	51.4
With addition of several drops of alcoholic sodium ethylate	90-100	30 min.	B	57.6

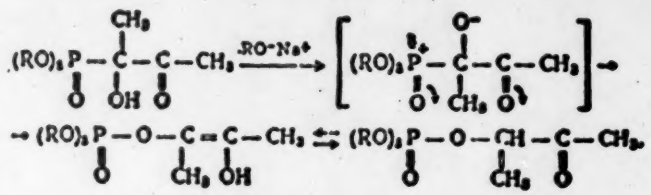
method. The i. r. spectrum of this product had an intense absorption band in the region of 3290 cm^{-1}, which is characteristic of OH groups in α-hydroxyalkanephosphonates [9]. These data are quite persuasive proof that Product A is an ester of α-hydroxy-β-acetoethanephosphonic acid.

Although the i. r. spectrum of Product B was quite similar to that of Product A, absorption in the region of 3250-3300 cm^{-1} was, nevertheless, absent. Tserevitinov's method failed to indicate the presence of a hydroxyl group in this product. Upon saponification of Product B with barium hydroxide, the barium salt of diethyl phosphate was obtained; consequently, we have in this case the mixed diethyl 3-keto-2-butyl ester of phosphoric acid.

The reaction dialkyl phosphites + biacetyl yields one of two isomers depending on reaction conditions



It is well known that the condensation of dialkyl phosphites with aldehydes and ketones is catalyzed by the alcoholates of the alkali metals [10]. When the interaction of dialkylphosphites with biacetyl was carried out in the presence of sodium alcoholate, the reaction was accelerated, and the mixed diethyl 3-keto-2-butyl ester of phosphoric acid was formed exclusively. It was further found that esters of α-hydroxy-α-acetoethanephosphonic acid on prolonged heating in alcoholic solution in the presence of sodium alcoholate are converted to the isomeric phosphates. A possible mechanism for the conversion is that esters of α-hydroxy-α-acetoethanephosphonic acid under the influence of sodium alcoholate and the electronegative carbonyl group split out a proton from the hydroxyl group and yield thereby a complex negative ion which has a positive charge on the phosphorus atom in the atom in the presence of the sodium atoms



Subsequently nucleophilic attack of the negatively charged oxygen atom on the neighboring positively charged phosphorus atom leads to the formation of the mixed ester of phosphoric acid. Accompanying elimination of a halide ion, as proposed by Bengelsdorf [5], is optional. The presence of electron-attracting atoms, such as the carbonyl group, is sufficient.

We have thus discovered an interesting new rearrangement of esters of α-hydroxy-α-acetoethanephosphonic acids to the isomeric mixed esters of phosphoric acid; the rearrangement occurs in alcoholic solution in the presence of sodium alcoholate and also during the action of dialkyl phosphites on biacetyl at a temperature of 125-130°.

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A NEW METHOD FOR THE SYNTHESIS OF UNSYMMETRICAL ACYL PEROXIDES

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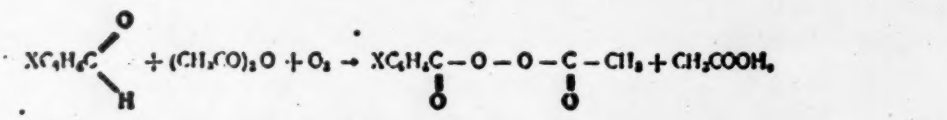
Symmetrical acyl peroxides, RCOOOCOR, which are widely used as polymerization initiators, are prepared by the interaction of acyl chlorides (or anhydrides) with sodium peroxide or hydrogen peroxide in the presence of a base [1, 2]. The reaction is carried out either in solution or in the absence of a solvent, and, generally, no difficulties are encountered in the preparation. Symmetrical peroxides have now been studied in considerable detail. Unsymmetrical peroxides have been studied considerably less, owing to the lack of a satisfactory method for their preparation. They are usually prepared by the interaction of a per acid with an acyl chloride. In addition, there is another method for the preparation of acetyl benzoyl peroxide only; in this method, benzaldehyde and acetic anhydride are poured onto sand and held under diffuse light for 3-4 days; this results in relatively low and varying yields of the peroxide [3]. Owing to the use of acetyl benzoyl peroxide in industry, a number of improvements in the method of preparation have been proposed [4, 5]. The Czechoslovakian authors F. Juracka and R. Chromecek [6] have made a particularly thorough study of the conditions under which this reaction is carried out.

In the present work, we have established that unsymmetrical acyl peroxides are formed in high yields by air oxidation of a mixture consisting of an aromatic aldehyde and acetic anhydride (in a molar ratio of 1:3).



(where X is p-CH_3O, p-Cl, or m-Cl). The yield of peroxide is 53-88%, on the basis of 100% pure product.

The oxidation was carried out at 30-40° in the presence of anhydrous sodium acetate (0.2-0.3% of the substances used) or calcium carbonate (10-15%); the air flow rate was 2.5-3 liters/minute, and illumination was with a 75-watt lamp. The oxidation time was 3-6 hours, at the end of which the peroxide content had reached 30-40%. Samples were taken periodically to check the accumulation of peroxide. When the reaction was complete, the mixture was poured into water, the acetic anhydride was hydrolyzed, and the peroxide separated in the form of a white crystalline mass. After the raw product had been washed with a solution of soda and with water and dried, the peroxide content was 81-95%. All of the peroxides prepared in the present work were readily soluble in organic solvents, benzene, ether, carbon tetrachloride, chloroform, alcohol, petroleum ether, and acetic acid. They were explosive, and flared up when introduced into an open flame.

Acetyl p-chlorobenzoyl peroxide (I). Yield, 83%. Molecular weight, 208 (calculated for $C_9H_7O_4Cl$, 214.5). The peroxide content of the pure sample was 99.7% (iodometrically [7]). The m. p. was 49.5° (from petroleum ether).

Acetyl p-methylbenzoyl peroxide (II). Yield, 53%. Molecular weight, 187 (from benzene) (calculated for $C_{10}H_{10}O_4$, 194). The peroxide content of the pure sample was 99.5% (iodometrically). The m. p. was 65-65.5° (from petroleum ether).

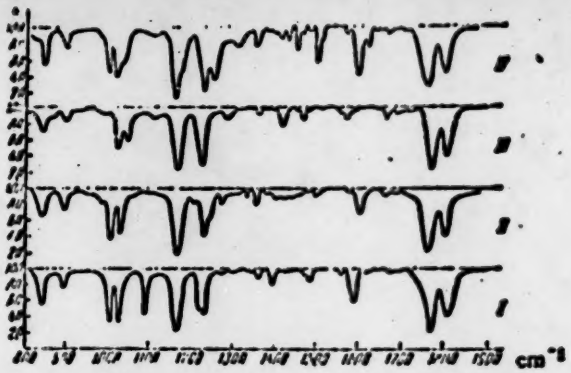


Fig. 1. Infrared transmission spectra: I) acetyl p-chlorobenzoyl peroxide, II) acetyl p-methylbenzoyl peroxide, III) acetyl m-chlorobenzoyl peroxide, IV) acetyl p-methoxybenzoyl peroxide.

Acetyl m-chlorobenzoyl peroxide (III). Yield, 88%. Molecular weight, 198 (calculated for $C_9H_7O_4Cl$, 214.5). The peroxide content of the pure sample was 98.5% (iodometrically). The m. p. was 53-54°.

Acetyl p-methoxybenzoyl peroxide (IV). Yield, 64%. Molecular weight, 190 (calculated for $C_{10}H_{10}O_5$, 210). The peroxide content of the pure sample was 96.5% (iodometrically). The m. p. was 59.5° (from petroleum ether).

The infrared spectra of peroxides (I), (II), (III), and (IV) were obtained using an ISK-11 instrument equipped with an NaCl prism; 0.1 M solutions in CCl_4 were used, and the cell thickness was 0.1 mm. All of the spectra were similar and possessed a series of characteristic bands (Fig. 1).

All of the spectra contained three bands in the region of 800-1060 cm^{-1}; one of these bands was weak and had a maximum at 899-900 cm^{-1}, while the two strong bands had maximums in the 1000-1030 cm^{-1} and 1020-1050 cm^{-1} regions. The positions of the maximums of these bands are the same in the spectra of (I) and (II), while they are shifted toward higher frequencies in the spectrum of (III) and toward lower frequencies in the spectrum of (IV). These bands can obviously be assigned to frequencies of the substituted benzene ring.

A band of average intensity with a maximum in the region of 840-842 cm^{-1} was present in all of the spectra, and there was almost no change in the position of the maximum or in intensity from one spectrum to the other. Some investigators have assigned this band to ν O-O vibrations [8]. In our case, the presence of a substituent in the benzene ring had no effect on the position of this band in any of the spectra, while the presence of a substituent did have an effect on the other bands.

In the spectrum of (I), there was a band of average intensity with a maximum at 1092 cm^{-1}, which was absent from the spectra of (II), (III), and (IV). The band in the region of 1150-1200 cm^{-1} with a maximum at 1170 cm^{-1} must be due to vibrations of the $-C-C-$ skeleton in the $-C-CH_3$ group. The band in the 1200-1270 cm^{-1} region in the spectrum of (I) was divided at the maximum, in the spectrum of (II) there was an inflection point, in the spectrum of (III) there was a single band, and in the spectrum of (IV) there were two distinct bands. These bands are obviously due to vibrations of the "oxygen bridge", C-O-O-C, (ν C-O). Hence, the interaction of the $-O-CH_3$ and C-O-O-C group vibrations readily explains the presence of the two bands in the spectrum of (IV). The band of average intensity in the 1580-1620 cm^{-1} region in the spectra of (II) and (IV) and the band in the 1550-1610 cm^{-1} region in the spectra of (I) and (III) may be assigned to benzene ring vibrations. The two strong bands in the 1750-1840 cm^{-1} region are assigned to C = O vibrations. The interval between the band maximums in these spectra was of the order of 38 cm^{-1}. These results are in good agreement with the data presented in reference [9]. The weak band in the 1350-1380 cm^{-1} region with a maximum at 1360 cm^{-1} is due to $-C-CH_3$ symmetrical vibrations.

Ultraviolet absorption spectra of 0.01 M solutions of these peroxide compounds in CCl_4 are shown in Fig. 1; these spectra were taken in the region of 233-305 mμ using an SF-4 instrument.

A strong absorption band with maximums at 245 and 243.5 mμ was found in the spectra of (I) and (II); absorption maximums found in the region of 246-247 mμ respectively, were less clearly expressed. Absorption in the long-wave-length region was identical for both compounds; there was a diffuse maximum at 270-273 mμ and a sharper maximum at 283 mμ. The spectrum of (III) contained no maximum in the 240-250 mμ region. Evidently, the band lay in the shorter wave-length region of the spectrum. There were two maximums, at 285.5 and 294 mμ, in the long-wave portion of this band. The spectrum of (IV) had only a single broad band with a maximum at 260 mμ. No additional absorption maximums were found in the long-wave portion of this band.

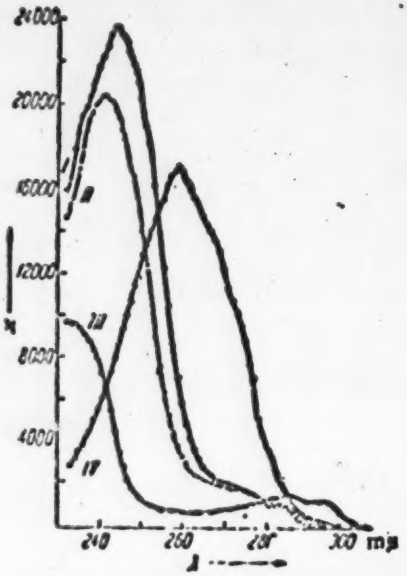


Fig. 2. Ultraviolet absorption spectra of organic peroxides. I) acetyl p-chlorobenzoyl peroxide, II) acetyl p-methylbenzoyl peroxide, III) acetyl m-chlorobenzoyl peroxide, IV) acetyl p-methoxybenzoyl peroxide.

None of the compounds absorbed appreciably in the region above 300 mμ. The interpretation of the remaining bands in the infrared and ultraviolet spectra requires additional experimental material, and will be presented in a future paper.

In addition to the peroxides described above, we also prepared, in 60% yield, acetyl 2,4-dimethylbenzoyl peroxide by oxidation of 2,4-dimethylbenzaldehyde; however, the purity of the peroxide was only 87%. It was a liquid with a freezing point of -7°. Treatment with concentrated HNO_3 and with bases did not increase the peroxide content of this sample. With the aim of extending this method of synthesizing unsymmetrical acyl peroxides, the oxidation of benzaldehyde in propionaldehyde was studied, and peroxides were formed in this case also. Work on the application of this reaction to other aldehydes and acid anhydrides continues.

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SYNTHESIS OF α,α-DI(CYANOALKYL)TETRAALKYLDISILOXANES

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It is well known [1-3] that in organosilicon nitriles of the type $\equiv Si(CH_2)_nCN$, where $n \geq 2$, (A), the CN group is very reactive and can be converted into various functional groups, for example, $-COOH$, $-NH_2$, $-COR$, etc. By analogy to the organic nitriles, which serve as starting material for the synthesis of bifunctional compounds such as diamines, dicarboxylic acids, amino acids, etc., it would be expected that organosilicon compounds having two (A) fragments in the molecule could also be used as a raw material for the preparation of α,ω-bifunctional compounds useful for the synthesis of organosilicon polymers.

In the present paper, we report on the synthesis of type (B) α,ω-dinitriles

$$\Phi-(CH_2)_n-\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{Si}}-O-\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{Si}}-(CH_2)_n-\Phi,$$

where n is 2 or 3, R and R' are CH_3 and C_2H_5, and Φ is $-CN$ or $-OCH_2CH_2CN$.

Considering that dihydrodisiloxanes of the type $HR_2SiOSiR_2H$ add to a number of olefinic compounds [4], we first attempted to prepare (B) nitriles by the addition of 2 moles of allyl cyanide to $HR_2SiOSiR_2H$ with the aid of Speir's catalyst [7]. However, these reactions did not take place (Table 1, Experiments 5 and 6). On the other hand, ethylmethylchlorosilane did add to cyano-containing olefins ($CH_2 = CH - CH_2CN$ and $CH_2 = CHCH_2 - O - CH_2CH_2CN$) (Table 1, Experiments 3 and 7), and we were able to synthesize the desired α-ω-nitriles by hydrolysis of the resulting monochlorides:

$$2\Phi CH_2CH_2CH_2Si(CH_3)(C_2H_5)Cl \xrightarrow[25^\circ]{H_2O} [\Phi CH_2CH_2CH_2Si(CH_3)(C_2H_5)]_2O,$$

where $\Phi = CN$; $-OCH_2CH_2CN$.

Water was used as the hydrolyzing agent. When concentrated HCl was used and the reaction was carried out under more vigorous conditions, the corresponding α,ω-dicarboxylic acid was obtained. It was also of interest to use the available γ-cyanopropylalkyldichlorosilanes for the preparation of dinitriles (Table 2, Experiments 1 and 2). We made use of the circumstance that the $-SiCl$ bond is more reactive toward Grignard reagents than is the $-C\equiv N$ bond [1,2], and accomplished the synthesis of Type (B) dinitriles according to the scheme.

$$NCCH_2CH_2CH_2SiRCl_2 \xrightarrow{R'MgCl} \xrightarrow{H_2O} [NCCH_2CH_2CH_2SiRR']_2O$$

for $R = R' = CH_3$; $R = C_2H_5$ and $R' = CH_3$; $R = R' = C_2H_5$.

$[NCCH_2CH_2Si(C_2H_5)_2]_2O$ was also prepared for $Cl_3SiCH_2CH_2CN$ by a similar reaction. The starting material, $Cl_3SiCH_2CH_2CN$, can be prepared easily at the present time. Thus, in the present work we showed that an active catalyst for the reaction

$$Cl_3SiH + CH_2{=}CHCN \rightarrow Cl_3SiCH_2CH_2CN$$

is the readily available N,N-diethylaniline, which allows the reaction to be carried out by refluxing the reaction mixture at atmospheric pressure in a flask fitted with a reflux condenser. There is also a patent [5] in which it is proposed to use $(n\text{-}C_4H_9)_3N$ as a catalyst for this reaction. A communication by Speir [6], which appeared after

TABLE 1

Expt. No.	Hydrogen-containing compound (h. c.)	Wt. of h.c., g/mole	Wt. of cyano-contg. olefin, g/mole	End b. p. of mixture, °C	Refluxing time, in hr	Yield of addn. prod. g	Yield of addn. prod. % **
1	CH_3SiCl_2H	94.5/0.82	[I] 55.0/0.82	128	5.5	132	83.4
2	$C_2H_5SiCl_2H$	130/1.16	[I] 73.0/1.16	160	6	206	90.5
3	$(C_2H_5)(CH_3)SiClH$	68/0.44	[I] 29.7/0.44	103***	28	22	28.6
4	$(C_2H_5)_2SiClH$	61/0.5	[I] 33.5/0.5	108****	20	Starting materials recovered	
5	$(HCH_2)(C_2H_5)Si)_2O$	72/0.135	[I] 27.4/0.41	120—117****	10	The same	
6	$(HC_2H_5)_2SiO$	30/0.138	[I] 18.7/0.28	121****	24	"	"
7	$(CH_3)C_2H_5)SiHCl$	20.8/0.19	[II] 22.4/0.20	110	3.5	34.9	78.6

*[I], allyl cyanide; [II], β-cyanoethyl allyl ether.

** Based on hydrosilane charged.

*** The boiling point of the mixture remained at 120-123° for a period of 20 hours, and decreased to 99.5° only after the addition of the last portion of $(CH_3)(C_2H_5)SiHCl$; only about 18 g of unreacted $CH_2 = CHCH_2CN$ was recovered in this experiment.

**** The temperature did not change during the entire heating period.

the completion of the present work, also recommends the use of N,N-dialkylamides as catalysts.

The cyano-containing olefins were added to the hydrogen-containing silanes by refluxing the reaction mixture in a flask according to the method of Speir [7] (in the presence of an 0.1 N solution of H_2PtCl_6 in isopropyl alcohol). The results of the experiments are presented in Table 1; the properties of the nitriles and dinitriles obtained are presented in Table 2.

EXPERIMENTAL

Sym-di(γ-cyanopropyl)diethyldimethyldisiloxane. 1) From γ-cyanopropylmethylethylchlorosilane. 19.3 g of this chloride and 25 ml of H_2O were stirred at room temperature for 5 hours; the organic layer was extracted with ether, and the aqueous layer was washed with ether. The ether extracts were combined, washed with a solution of soda and with water, and dried with anhydrous Na_2SO_4 for a day. The ether was distilled, and from the heavy residue was isolated 10.3 g of $(NCCH_2CH_2CH_2Si(CH_3)(C_2H_5))_2O$ with a b. p. of 195-197° (3 mm).

2) From γ-cyanopropylethyldichlorosilane. CH_3MgCl, prepared from 12.1 g (0.5 g-atom) of magnesium in 700 ml of ether, was added over a 4-hour period to a solution of 75 g of $(NCCH_2CH_2CH_2)(C_2H_5)SiCl_2$ in 700 ml of ether; the reaction flask was cooled with ice during the addition. The mixture was stirred at room temperature for another 5 hours; it was then decomposed with water, and stirred for an additional hour. The usual treatment yielded 28.7 g of $(NCCH_2CH_2CH_2Si(CH_3)(C_2H_5))_2O$ with a b. p. of 179-184° (3 mm) and n_D^{20} 1.4515. Methylmagnesium chloride (from 14.8 g, 0.57 g-atom of magnesium) was added over a 50-minute period to an ether solution of 75 g (0.385 mole) of γ-cyanopropylethyldichlorosilane, and, after the usual treatment, 18 g of $(NCCH_2CH_2CH_2Si(C_2H_5)(CH_3))_2O$ and 22 g of $NCCH_2CH_2CH_2Si(C_2H_5)(CH_3)_2$ were obtained; the latter compound had a b. p. of 66-68° (3 mm).

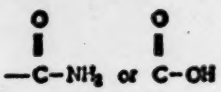
Sym-di(γ-cyanopropyl)tetramethyldisiloxane. CH_3MgCl, prepared from 14.7 g (0.6 g-atom) of Mg, and 82 g (0.45 mole) of $NCCH_2CH_2CH_2Si(CH_3)Cl_2$ were used in reaction. From the reaction mixture were separated 18.9 g of $NCCH_2CH_2CH_2Si(CH_3)_2$ with a b. p. of 79-80° (16 mm), n_D^{19} 1.4273, d_4^{20} 0.8244 and 14 g of $(NCCH_2CH_2CH_2Si(CH_3)_2)_2O$ with a b. p. of 161-162° (1.5 mm).

TABLE 2

Expt. no.	Substance	B. p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc. [8]	Elemental analysis, % found Si	found C	found H	found Cl	calc. Si	calc. C	calc. H	calc. Cl
1	$NCCH_2CH_2CH_2Si(C_2H_5)Cl_2$	90/3	1,4625	1,1295	47,8	47,8				36,2 36,2				36,2
2	$NCCH_2CH_2CH_2Si(C_2H_5)(CH_3)Cl$	121/4	1,4515	0,9805	47,9	48,2				20,3 20,4				20,2
3	$NCCH_2CH_2CH_2Si(C_2H_5)(CH_3)_2$	66,3	1,4363	0,8377	48,5	48,5	17,5 17,8	62,1 61,9	11,1 11,2		18,1	61,9	11,0	
4	$NCCH_2CH_2OCH_2CH_2CH_2Si(CH_3)(C_2H_5)Cl$	123,1	1,4355	1,0098	59,0	59,2	12,2 12,3	49,6 49,5	8,2 8,3	14,3 14,2	12,7	49,2	8,2	16,1
5	$[NCCH_2CH_2Si(C_2H_5)_2]_2O$	175/2	1,4605	0,9470	85,8	85,2	18,3 18,6				18,9			
6	$[NCCH_2CH_2CH_2Si(CH_3)_2]_2O$	161—2/2	1,4441	0,9344	76,3	76,4	20,0 20,0	34,1 34,2	9,2 9,1		20,9	53,7	9,0	
7	$[NCCH_2CH_2CH_2Si(CH_3)(C_2H_5)]_2O$	193/3	1,4513	0,9377	85,2	85,5		56,8 57,0	9,5 9,7			56,7	9,5	
8	$[NCCH_2CH_2CH_2Si(C_2H_5)_2]_2O$	193/1,5	1,4503	0,9413	94,3	94,2		60,4 60,6	10,2 10,1			59,2	9,9	
9	$[NCCH_2CH_2OCH_2CH_2CH_2Si(CH_3)(C_2H_5)]_2O$		1,4552	0,9741	107,2	107,8		55,6 56,0	9,8 9,6			56,2	9,4	

Sym-di(γ-cyanopropyl)tetraethyldisiloxane. C_2H_5MgCl (from 14.4 g, 0.6 g-atom, of magnesium) was added over a 1.5-hour period to an ether solution of 100 g (0.51 mole) of $(NCCH_2CH_2CH_2)C_2H_5)SiCl_2$. After the usual treatment, vacuum distillation yielded: Fraction 1, 115-125° (2 mm); Fraction 2, 182-192° (2 mm). The substance of Fraction 1, the silanol $NCCH_2CH_2CH_2Si(C_2H_5)_2OH$, evolved water on standing in air; this substance was heated at 100° for 2 hours, dried over anhydrous Na_2SO_4, combined with Fraction 2, and the mixture was again distilled. $(NCCH_2CH_2CH_2Si(C_2H_5)_2)_2O$ was obtained at a temperature of 190-193° (1.5 mm).

Sym-di(γ-(β-ethoxy)propyl)diethyldimethyldisiloxane. 8.1 g of $NCCH_2CH_2OCH_2CH_2CH_2$-$Si(CH_3)(C_2H_5)Cl$ and 25 ml of water were stirred for 2.5 hours at 20° and for 0.5 hours at 35-40°. The mixture was cooled, twice extracted with ether, dried then treated in the usual manner. The ether was distilled, and the heavy residue was heated under vacuum at 120-140° and 0.5 mm for several minutes; the product did not distill. The resulting light yellow oil (6.3 g) had a molecular weight of 392 (cryoscopic method in benzene); calculated for $C_{18}H_{36}O_3N_2Si_2$, 384.6. A band at 2256 cm^{-1}, characteristic of the $-C\equiv N$ group, was present in the infrared spectrum of this substance; frequencies corresponding to:



vibrations were not present.

Sym-di(γ-(β-carboxyethoxy)propyl)diethyldimethyldisiloxane. 22 g of $NCCH_2CH_2$-$OCH_2CH_2CH_2Si(CH_3)(C_2H_5)Cl$ and 55 ml of concentrated HCl were stirred at 60-80° for 4 hours; another 25-30 ml of concentrated HCl was then added, and the mixture was stirred for an additional 0.5 hour at 80-90°. On the following day, the precipitated NH_4Cl crystals were separated from the mixture, which was then extracted three times with ether. After the usual treatment, the yellow-brown oil (19.8 g) was heated at 0.5 mm to 120-140°; the substance did not destill. 0.3103 g of this oil in solution in alcohol was titrated with 41.7 ml of 0.1 N NaOH solution (methyl orange end point); calculated for $(HOOCH_2CH_2OCH_2CH_2CH_2Si(CH_3)(C_2H_5))_2O$ - 44.5 ml. The infrared spectrum confirmed the structure proposed for this substance.

β-Cyanoethyltrichlorosilane. 160 g of acrylonitrile and 90 g of N,N-diethylaniline were charged to a flask fitted with a reflux condenser, a thermometer, and a dropping funnel, and the mixture was heated for 8 hours while 410 g of technical $HSiCl_3$ (containing 5-7% $SiCl_4$) was added. The contents of the flask were then refluxed for an additional 32 hours, the temperature increasing from 42.5 to 87° during this period. The light products, including 45 g of acrylonitrile, were distilled in a column with an efficiency of 20 theoretical plates, and the residue was fractionated under vacuum. 385 g of a fraction boiling at 90-98° (15 mm) was collected; this consisted of $Cl_3SiCH_2CH_2CN$ and $(C_2H_5)_2NC_6H_5$, which partially crystallized. 73 g of liquid, which consisted chiefly of $(C_2H_5)_2NC_6H_5$, was separated by freezing the mixture, and the residue consisted of crystals of $Cl_3SiCH_2CH_2CN$ with an m. p. of 26-30°. The melting point of a mixture with β-cyanoethyltrichlorosilane, prepared by direct synthesis [1] (m. p. 32-34°), was 28-31°.

Sym-di(β-cyanoethyl)tetraethyldisiloxane was prepared by the method described above using a molar ratio of reactants of 2.3 moles of ethylmagnesiumchloride (calculated on the magnesium) per mole of β-cyanoethyltrichlorosilane.

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THE USE OF INDUCED α-PARTICLES FROM ARTIFICIAL RADIOACTIVITY FOR THE QUANTITATIVE CONTROL OF PRODUCTS CONTAINING ALUMINUM AND BORON

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Artificial radioactivity, induced α-particles, has previously been used for the analysis of biological tissues [1].

We now propose a rapid method for the analysis of powdered samples containing aluminum and boron using Po^{210} as an alpha emitter; this method is useful in connection with process control in the processing of ores.

The nuclear reaction (α, n) resulting when boron B^{10} is bombarded with alpha particles forms the radioactive nitrogen isotope N^{13}. Decomposition of the N^{13} ($T\ ^1/_2$ = 10.1 minutes) yields positrons with a maximum energy of 1.24 Mev. The nuclear reaction resulting when Al^{27} is bombarded with alpha particles (α, n) yields the radioactive phosphorus isotope P^{30}. Decomposition of the P^{30} ($T\ ^1/_2$ = 2.5 minutes) yields positrons with a higher maximum energy – 3.6 Mev.

The Po^{210} used as an alpha emitter had an activity of 120 μc.

Activity was induced in the B- and Al-containing products by bombardment with alpha particles for 10 minutes. At the end of this time, the P^{30} (product of the bombardment of aluminum) had increased to 0.94 of the maximum value. At the end of the same period, the N^{13} activity had increased to 0.5 of the maximum value.

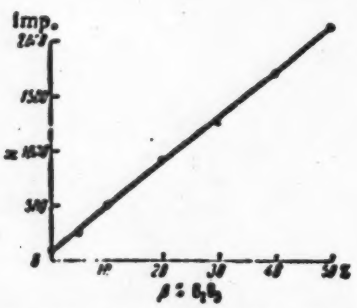

Fig. 1. Calibration curve for mixture of hydroboracite and gypsum.

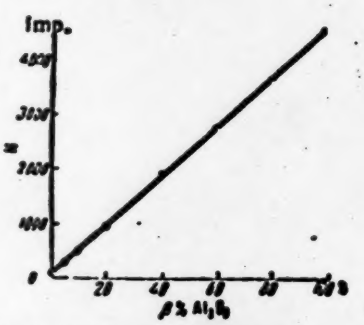

Fig. 2. Calibration curve for mixtures of aluminum oxide with quartz.

An activation time of 10 minutes for boron sets the time requirement for this rapid method of analysis.

A minimum distance between the source of alpha particles and the control sample (0.5 mm) decreases the loss of energy by the alpha particles in air. After activation by alpha particle bombardment, the sample was

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placed under an end window counter. The time interval between the activation and the beginning of counting must be a minimum and constant. The induced radioactivity was recorded on a B-2 instrument. For the determination of the boron and aluminum contents of control samples, calibration curves were constructed using standard samples with known boron and aluminum contents.

The calibration curve for hydroboracite ($CaO \cdot MgO \cdot 3B_2O_3 \cdot 6H_2O$) is shown in Fig. 1. The bombardment of Mg^{25} results in a nuclear reaction (α, p) which yields the radioactive isotope Al^{28}; this isotope emits electrons with a maximum energy of 3.0 Mev and has a half-life of 2.3 minutes.

Owing to the positron-electron activity induced in the hydroboracite, the activity recorded was the sum of that of the N^{13} and the Al^{28}. The activity of the Al^{28} is considerably less than the activity of the N^{13}, because the amount of magnesium in hydroboracite is small and the yield of the nuclear reaction (α, p) is also small.

Emission from the Al^{28} does not disturb the direct proportionality between the count of the induced activity and the hydroboracite content of the control sample, since the magnesium is present in the crystal lattice of the hydroboracite.

As may be seen from the calibration curve (Fig. 2), the present method can be used for the determination of aluminum oxide content within the range 1-100%.

Other radioactive elements formed by nuclear reactions resulting from the Po^{210} alpha particles have either a long or very short half-life and do not have an appreciable effect on the count during the analysis for boron and aluminum.

The range of the Po^{210} alpha particles in the sample to be analyzed is about 20 μ, the weight of the sample has no effect on the amount of induced radioactivity. This makes it possible to use very small amounts of the product for the analysis (1 g and less).

The present method is rapid, and the accuracy of the determination of boron and aluminum in rich ores, beneficiation products, and alloys is sufficient for process control.

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ON THE REDUCTION OF COPPER FERRITE WITH GRAPHITE

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Copper ferrite, $CuFe_2O_4$, has a tetragonal lattice at room temperature [1, 2]. At temperatures above 760°, it has the structure of a spinel. The latter structure can be fixed by rapid cooling [3]. The nature of the bonding forces between the ions changes during the transition from one form to the other [4, 5]. Covalent bonding, which plays a considerable role in the lattice of tetragonal ferrite, becomes weaker in cubic ferrite, in which ionic bonding is the major form.

The kinetics and the mechanism of the reduction of tetragonal and cubic copper ferrites by graphite under vacuum was investigated in the present work. The reducing agent was graphite prepared by grinding Acheson electrodes and calcining first at 1200° in a graphite crucible without access of air and then under vacuum at 1000°.

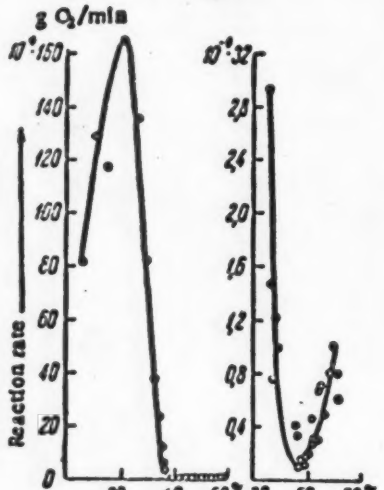

Fig. 1. Dependence of the rate of reduction of tetragonal copper ferrite by graphite on percent reduction at 90°.

The original ferrite was prepared by annealing a mixture having the composition $CuO \cdot Fe_2O_3$ in air at 1000° for 30 hours. For the preparation of ferrite with a tetragonal lattice, the sintered products were held for 3 hours at 700° and then cooled in the furnace. The cubic form of ferrite was obtained by quenching in water immediately after the annealing. Data obtained by x-ray analysis of the samples were in agreement with those in the literature [5].

A weighed portion of the ferrite was carefully mixed and ground with graphite. The reduction experiments were carried out in a vacuum apparatus [6] employing quartz spring scales. The gases evolved were continuously pumped off with high-vacuum pumps. The method by which the experiments were carried out permitted continuous analysis of the gaseous reaction products by means of three traps which were connected in parallel and immersed in liquid nitrogen. The carbon dioxide evolved during the course of the reaction was frozen alternately in one trap after the other. The amount of carbon monoxide was determined from the difference between the loss in weight and the amount of CO_2. The percent reduction was calculated from the amount of oxygen removed from the sample.

Reduction of the copper ferrite was carried out at temperatures both below the transition point (650, 700, and 750°) and above (800, 900, and 1000°). The kinetic curves for the reduction of tetragonal copper ferrite are presented in Figs. 1 and 2. Only a small per cent reduction was obtained at temperatures below 900° (respectively, 11, 18, 24, and 35%), and the process practically ceased when these values were attained. At 900 and 1000°, there was 100% reduction of the samples. The first stage of the reduction was characterized by a maximum in the reaction rate, which then dropped sharply and became very low at 40-50% reduction. However, after 50% reduction there was

an increase in the reaction rate, as is clear from the section of the kinetic curve between 30 and 70% reduction; this portion of the curve is plotted on larger scale on the right side of Fig. 2.

X-ray investigation of the solid reduction products showed that at temperatures of 650, 700, and 750°, the products of incomplete reduction consisted of copper, a spinel phase, and the remains of the original tetragonal ferrite. The spinel phase in this case could be either magnetite or cubic ferrite, the lattice parameters of which are so close that it is impossible to distinguish between them by ordinary methods of phase analysis. The x-ray patterns of these samples showed, however, that a considerable amount of copper was present in the reduction products as an independent phase, and therefore the copper could not be a part of the spinel. Therefore, it may be assumed that the spinel phase in these samples was magnetite, possible containing some dissolved copper.

Figure 3 compares the kinetic curves showing the dependence of the reduction rates of the tetragonal and cubic forms of ferrite on the degree of reduction at temperatures of 700, 800 and 1000°. (The curve for 800-1000° was obtained by continuing the reduction at 1000° after a preliminary reduction at 800°). Figure 3 shows that at

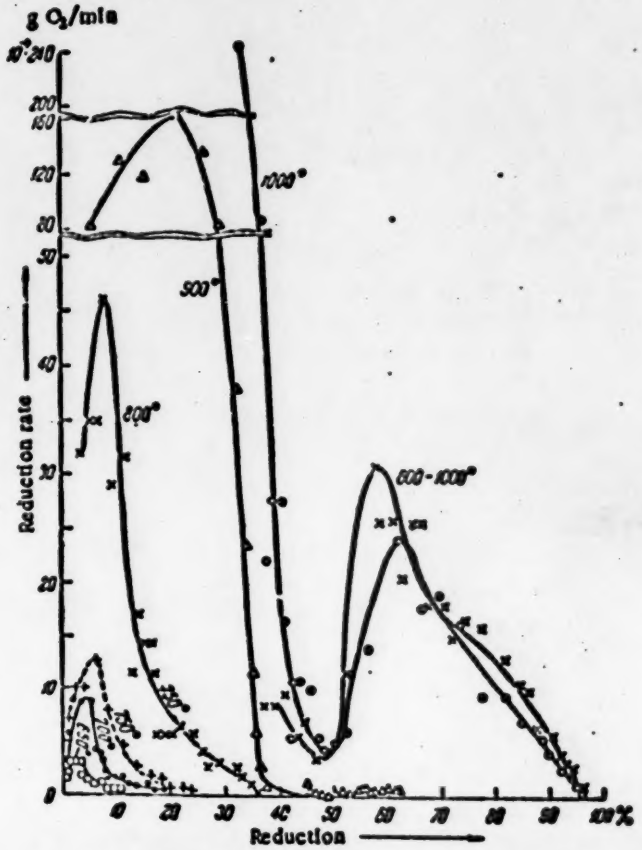

Fig. 2. Dependence of reduction rate of tetragonal copper ferrite by graphite on percent reduction at various temperatures (th curve for 800-1000° was obtained by reduction at 1000° of a sample which had first been reduced 35% at 800°).

the same temperatures, the rate of reduction of cubic ferrite is lower than that of tetragonal ferrite. Moreover, the maximum in the reaction rate was not found in the first stage of the reduction of cubic ferrite. Subsequent stages in the reduction of the two forms were identical. The gaseous reaction products consisted of a mixture of

CO and CO_2. The CO_2 content in the initial stage of the process was 60-65%. It gradually decreased as reduction proceeded. After 70% reduction, the gaseous phase consisted of practically pure carbon monoxide.

In the x-ray patterns of the samples obtained by 13 and 30% reduction at 900°, there were also present lines characteristic of the patterns of copper, spinel, and tetragonal ferrite. In these cases, the spinel component of the sample was apparently a mixture of magnetite and cubic ferrite. The latter was formed at this temperature from tetragonal ferrite as a result of a phase transformation. In the samples reduced to a higher per cent reduction at 900°, the lines characteristic of tetragonal ferrite disappeared, and lines due to wüstite and iron appeared. Upon complete reduction copper and iron were found in the solid phase.

It should be pointed out that copper prepared by reduction of tetragonal ferrite at a temperature above the transition point has a lattice parameter (3.599 A) somewhat lower than that given in the tables (3.608 A). When tetragonal ferrite was reduced at a temperature below the transition point and when cubic ferrite was reduced at a temperature above 760°, the resulting copper had a lattice parameter corresponding to that of pure copper. The low value of the lattice parameter of copper indicates the presence of a certain amount of dissolved iron. During the transformation of one modification of ferrite into the other, there is a change in the bonding forces in the

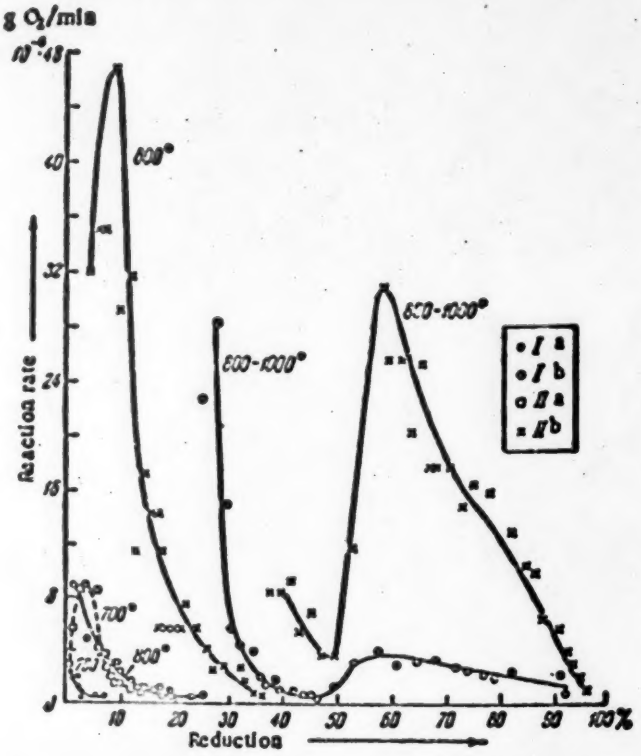

Fig. 3. Comparison of the kinetic curves for the reduction of cubic (I) and tetragonal (II) copper ferrites by graphite. a) at 700°, b) at 800°.

lattice, promoted, apparently, by the transfer of iron ions into the metallic phase. Proof of this is the fact that the temperature dependence of the lattice parameter of the copper varied in jumps which corresponded to the transition point.

The mechanism of the crystallochemical transformations of copper ferrite during reduction can be represented as follows: as oxygen is removed, an excess of iron and copper ions is formed at the surface; the copper,

which is the least stably bonded to oxygen, forms the metallic phase, while the iron diffuses into the depths of the ferrite particle, displacing the copper; a portion of the trivalent iron ions is converted to the divalent form due to the reduction process, and the ferrite lattice approaches the magnetite lattice. Then, as all of the ferrite is converted to magnetite, reduction of the magnetite begins according to the scheme proposed in reference [7].

Thus the reduction of cubic and tetragonal ferrites is a step-wise process:

$$CuFe_2O_4 \rightarrow Cu + Fe_3O_4;\quad Fe_3O_4 \rightarrow FeO;\quad FeO \rightarrow Fe.$$

The conversion of the tetragonal lattice of ferrite into the cubic form proceeds simultaneously with the reduction process and has an effect on the nature of the latter.

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